Environmental Assessment - CFR §25.31

for FAP 5A4440

1. **Date:** April 2, 1998

2. **Name of Applicant/Petitioner:** Lyondell-CITGO Refining Company Ltd.

3. **Address:** P. O. Box 2451, Houston, Texas 77252-2451

4. **Description of Proposed Action:** This request is to amend 21 CFR §172.878, to permit the use of White Mineral Oil, U.S.P., with a minimum viscosity of ISO 100, as a dust control agent at an application rate of no more than 800 ppm (0.08% by weight) on whole, unhulled (rough) rice. This proposed commercial application for White Mineral Oil on rough rice would be comparable with White Mineral Oil application for other commodity grains as described in CFR §172.878.

The current widely accepted practice of using White Mineral Oil to control grain dust has essentially eliminated the occurrence of explosions and fires at wheat and other grain handling facilities. In contrast to other grain handling facilities, rice handling facilities have never needed to control dust emissions because rice dust is not conducive to explosion or fire. However, recent federal regulations, which focus on suspended particulate in occupational settings and in the atmosphere, have changed all this. The need for the proposed action is to help rice handling facilities comply with the requirements of the Federal Clean Air Act Amendments of 1990, and to assist in reducing worker exposure to airborne dust at rice handling facilities.

Several rice handling facilities have tried using White Mineral Oil for dust control. However, due to the highly adsorptive nature of the protective outer rice hull, application of White Mineral Oil at the currently approved rate of 200 ppm does not effectively control rice dust. Lyondell-CITGO Refining Company Ltd. conducted a commercial study at a rice handling facility to determine if a higher application rate could control dust. Our field tests show that dust emissions at rice handling facilities can be controlled at the proposed application rate of 800 ppm.

Rice handling facilities where White Mineral Oil would be used as a dust control agent are located principally in the rice-growing states of the U.S. The sites where the rice handling facilities are located may be in industrial, urban, or rural areas. The environments at the sites of rice handling facilities are as varied as the locations themselves.

General Description of Environmental Effects and Biodegradation of White Mineral Oil

Environmental Effects

White Mineral Oil has certain physical and chemical characteristics which deem it harmless to the environment in negligible quantities. These include a vapor pressure less than 0.1 mm of Hg at 70°F, a water solubility value less than 0.1 wt.%, and a boiling range of 700° to 1050° F. In addition, White Mineral Oil is viscous and non-soluble in water, both advantages in a soil environment where leaching into the water table is a real concern. Its benign characteristics in conjunction with the relatively small amount of environmental introduction make White Mineral

Oil a viable option for rice dust suppression. The White Mineral Oil introduced into the environment due to the proposed action provides for the following environmental effects:

a) **Air**--Oil cannot be volatilized because of its extremely low vapor pressure. The only introduction into the atmosphere is the quantity of combustion products (carbon dioxide, water, and ash) of White Mineral Oil that is incinerated, rather than the White Mineral Oil itself, entering the air environment. The amount of carbon dioxide introduced into the atmosphere would be negligible and is not controlled by U.S. EPA. The estimated maximum amount of combustion products entering the atmosphere due to the proposed action would be 1478 tons per year via combustion of sewage sludge waste and rice hulls for biomass fuel (see Table 3). However, the proposed action would, in fact, *reduce* emissions at rice handling facilities by between 6,000 and 32,000 tons/yr. Moreover, the amount of smaller dust particles emitted to the air would be significantly reduced, since they adhere to the grain surface due to the White Mineral Oil, with a significant decrease in the amount of dust less-than-10 μm being discharged into the air.[1] Hence, using White Mineral Oil for dust suppression will decrease the amount of respirable dust which workers are subjected to, providing a safer working environment for employees and reducing the probability of workers developing respiratory problems. The worker health and safety benefits derived from the reduction of emissions at rice handling facilities appear to outweigh the comparatively insignificant quantity of combustion products due to the proposed action.

b) **Land**--There would be no effect on ground composition since the White Mineral Oil would be biodegraded to carbon dioxide and water, and the resultant negligible carbon dioxide component would find its way into the atmosphere, nor would it cause changes to the terrestrial ecosystem since the small amount of carbon dioxide, even if re-introduced into the ground via rainfall, would be insignificant. The uncontrolled route of White Mineral Oil introduction through animal excretion due to the proposed action could add 902 tons per year of White Mineral Oil into U.S. soils, (See Table 3). Based upon the most conservative biodegradation range of 25 to 60% for White Mineral Oil, approximately 225 to 540 tons of the 902 tons will biodegrade and release a negligible amount of CO_2 into the atmosphere.

c) **Water**--Any trace amount of White Mineral Oil permeating from landfill to sub-surface water or otherwise introduced to land surface water, prior to its biodegradation, would not produce deleterious matter in the water, nor adversely affect water quality, since White Mineral Oil is not miscible with water.

Biodegradability

Although White Mineral Oil cannot be proven to be 100% biodegradable, short-term trends of 25 to 60% biodegradability have been observed. White Mineral Oil will biodegrade to various degrees and within different time frames based upon the deposition point. Data is available for White Mineral Oil biodegradation as tested by the Modified Sturm OECD 301B 28-day test (tests for CO_2 released and dissolved organic carbon [DOC]) and the CEC L-33-T-82 21-day test (tests for IR absorption and CH_2-CH_3 loss). Data for biodegradation of White Mineral Oil is available from both types of tests, but will not provide precise ultimate degradation information because of the relatively short length of time compounds are analyzed. The Modified Sturm test shows mineralization of the product through to carbon dioxide, water and humic substances, and

[1] Wardlaw, Parnell, Lesikar, *Dust Suppression Results With Mineral Oil Applications for Corn and Milo*, ASAE Paper #87-6550, page 1.

as a result, only shows complete oxidation. The CEC test applies to most organic compounds, determining the overall biodegradability of the hydrocarbons by measuring all transformations that the material undergoes, including oxidation and hydrolysis. However, the CEC test does not measure oxygen consumption and extensive degradation of the product and carbon dioxide evolution through to mineralization, very important factors in the long-term biodegradation of an organic compound. Rather, it measures the breakdown of carbon chains via IR absorption.

Data from Modified Sturm and CEC L-33-T-82 correlate favorably. This is important because the tests complement each other whereby more parameters are covered using both sets of data.

The rates of biodegradation in the environment will vary based on many parameters such as the local substrate's microorganisms, pH, aeration/turnover rate, and aerobic vs. anaerobic (anaerobic decomposition is negligible) conditions, humidity and temperature.[2] These conditions cannot be accounted for in lab analyses, however. For example, hydrocarbon degradation by microbial communities depends upon the composition of the community and its adaptive response to the presence of hydrocarbons.

Another possible means of biodegradation of White Mineral Oil which cannot be accounted for in available tests is cometabolism--the microbial metabolism of a chemical which does not serve as a nutrient or energy source for that organism. In practice, co-oxidation can occur, whereby non-growth hydrocarbons are oxidized in the presence of hydrocarbons which serve as growth substrates. If this occurs, much greater biodegradation will be observed than would normally be anticipated. Obviously, cometabolism is not accounted for in the available test methods. And it is not known to what extent cometabolism contributes to the transformation of petroleum components in nature, nor the extent to which organisms may be manipulated to enhance this process. Although fecal material is a highly decomposed substrate, it contains an abundance of partially digested organic matter that provides a rich resource for specialized detritivores, in addition to bacteria, fungi, and earthworms, which will only benefit the biodegradation process. The complete study of biodegradation conducted by Lubrizol and referenced in this document, is provided herein as Attachment D.

General Description of Grain Dust Effects

As discussed in our original petition, the occupational safety issue is of primary importance and provides a significant impetus to alleviate or reduce inhalable and particularly, respirable particles from the workplace. Because rice husks contain 17 to 20% silica, and 19 to 23% ash,[3] respirable rice particles must be considered even more dangerous than particulate from other grains. Silica fibers of a certain size (1 to 10 μm) can be respired into the deepest areas of the lung, the alveoli, where they can impact and cause direct, localized damage such as tumors, silicosis (a serious lung condition similar to pneumoconiosis "dust in the lungs"), chronic bronchitis, bronchial asthma and emphysema. Particle sizes in the range of 3 to 15 μm can deposit in the upper respiratory system causing eye, nose, throat and lung irritation.

---

2 Stephanie Harold, *Biodegradability: Review of the Current Situation*, Lubrizol International Laboratories, Bleper, Derby, UK, April 1993.

3 R.K. Chawla, S.K. Goyal, and P.S. Panesar, "Design of Dust Control Systems for Rice Husk Fired Boilers", *Journal of Industrial Pollution Control*, 11, 1-11, (1995).

General Description of Disposal Routes of White Mineral Oil

We believe that disposal routes for White Mineral Oil as a component of edible rice and rice processing residue should not be limited to activities involving consumption of white rice by humans and the consumption of rice by-products, principally rice hulls, by animals. We believe that disposing rice hulls has been a long-standing problem for this agricultural by-product.[4] In addition to considering rice hulls as an animal feed supplement, we consider that a realistic assessment of alternative disposal practices for White Mineral Oil, as a component of rice processing residue after handling and milling for rough rice, may also include incineration, industrial or agricultural utilization, and landfill.[5] The general description of the locations and their environments at or adjacent to those locations where disposal of White Mineral Oil following its use is anticipated to occur follows:

a) **Human excreta**--Any White Mineral Oil as a component of rice and rice by-products consumed by humans is eliminated in excreta. Human consumption of White Mineral Oil as a component of edible rice, rice-derived products (e.g. alcoholic beverages), and foods that use rice-derived production aids (e.g. rice hulls as filter aids for fruit and vegetable juice filtration) is anticipated to occur at locations corresponding to the distribution of the U.S. population and in U.S. patterns of daily dietary intake. Human excreta are expected to undergo treatment in municipal sewage systems or septic tank systems. The White Mineral Oil will then become a part of sewage sludge that may be disposed, consonant with current environmental regulations, by incineration, co-disposed with municipal solid waste in landfills, or incorporated in surface land. In areas where there are municipal or governmental type sewage disposal plants, the excrement is settled and the White Mineral Oil content is separated, along with other sewage solids, usually in an emulsion form, and sent to a landfill for disposal. In the landfill, biodegradation occurs, producing carbon dioxide and water. In those areas where there is no municipal sewage disposal unit, the sewage is disposed of through a septic system.

b) **Animal excreta**--Any White Mineral Oil consumed by animals as a component of feed will be found in animal excrement. Animal consumption of White Mineral Oil as a component of rice by-products is anticipated to occur at agricultural locations throughout the U.S. Animal excreta containing the White Mineral Oil are anticipated to be distributed on agricultural land in patterns appropriate to the husbandry practices for livestock.

c) **Rice hull incineration**--Rice hulls containing White Mineral Oil as a component may be incinerated when used as a fuel for heating or electricity generation. Combustion of the White Mineral Oil component of hulls is anticipated to occur particularly at or near the rice-growing regions of California, Louisiana, Texas, Mississippi, Missouri, and Arkansas.

d) **Landfill disposal**--Rice processing waste containing White Mineral Oil may also be discarded directly to landfills. Any landfill disposal of White Mineral Oil as a component of rice processing waste is expected to occur in areas close to the rice handling facilities in the six principal rice-growing states.

---

[4] Kenneth B. Young, Gail L. Cramer, and Eric J. Wailes, *Prospects for Increasing Returns from Rice Bran and Other Rice Milling By-Products,* Arkansas Agricultural Experiment Station Special Report 152, University of Arkansas, Fayetteville, AR, September 1991.

[5] Bor S. Luh, "Rice Hulls," in *Rice, Vol II, Utilization,* 2nd, ed. Bor S. Luh Ed., Van Nostrand Reinhold, New York, 1991, pp. 269-294 (Chapter 12).

5. Identification of Chemical Substances that are the Subject of the Proposed Action:

White Mineral Oil is a colorless, odorless derivative of petroleum hydrocarbon, and is listed under the Chemical Abstract Service Registry as White Mineral Oil (Petroleum), and sold by LCR to the rice industry under the trade name Duoprime® Oil RD-H.* See Table 1.

Table 1. Identification of ISO 100 White Mineral Oil

Physical Description	Structural Formulae	Molecular Weight	C.A.S. Number	Additives & Impurities
• Colorless, odorless, liquid • Slightly combustible (flash pt. 232°C) • Viscous (ISO 100) • Non-carcinogenic • V.P. <1 mm HG	C_nH_{2n+2} and C_nH_{2n} Paraffin & cycloparaffin hydrocarbons, respectively	425	8042-47-5	None

*Duoprime® Oil RD-H (ISO 100) White Mineral Oil is produced by the Lyondell Lubricants Division of Lyondell-CITGO Refining Company Ltd (LCR), located at 12000 Lawndale, Houston, Texas 77017.

6. Introduction of Substances into the Environment:

The 1990/91 U.S. "rough" rice production was 158,100,000 cwt. At an application rate of 800 ppm White Mineral Oil, a maximum 6324 tons/yr White Mineral Oil could enter the environment as a result of the proposed action, as shown in Table 2.

Table 2. White Mineral Oil Calculated Use for 1990/91 U.S. Rough Rice Production Treated with 800 ppm

158,100,000 cwt. times 100 lbs per cwt. = 15,810,000,000 lbs rough rice

---

15,810,000,000 lbs rough rice times .08% wt (800 ppm) = 12,648,000 lbs White Mineral Oil

---

12,648,000 lbs White Mineral Oil divided by 2,000 lbs per ton equals

---

6324 tons White Mineral Oil

Routes of entry, quantities introduced (tons/year), and environments potentially affected are shown in Table 3.

Table 3. Introduction of White Mineral Oil into the Environment

Entry Route	Environment		
	Air	Land	Water
1. From use sites (Via unknown routes)			
a. Overspray loss waste	nil	1707[2/]	nil
b. Accumulated rice waste	nil	1731[2/]	nil
2. To disposal sites (Via human consumption)			
a. POTW waste	62[1/]	301	nil
b. Septic tank waste	27[1/]	129	nil
c. Unaccounted waste	-	35[2/]	-
(Via animal consumption)	nil	902	nil
(Via rice biomass fuel)	1389[1/]	nil	nil
3. Totals	1478	4846	nil

[1/]The estimate is the quantity of White Mineral Oil that is incinerated. Combustion products of White Mineral Oil, rather than the White Mineral Oil itself, enter the air environment.
[2/]Overspray loss and unaccounted use of unknown disposal quantities are assigned to land route of entry as the most probable environmental introduction on the basis of White Mineral Oil properties and manner of use.

Introduction into Environment at Production Sites

White Mineral Oil is currently being produced at LCR and at other U. S. refineries for other applications. The production sites are managed under EPA, the Texas Natural Resources Conservation Commission (TNRCC), as well as other state regulatory agencies, and OSHA and are in compliance with all requirements. There are no extraordinary circumstances which would require additional regulation of White Mineral Oil.

Introduction into Environment at Use Sites

Introduction at Sites via Application as a Dust Suppressant

The process for application of White Mineral Oil to rough rice would be the same as for other commodity grains. White Mineral Oil would be sprayed directly onto the rough rice in the enclosed area of the receiving pit or bucket elevator boot. Because White Mineral Oil is of ISO 100 viscosity, and has a vapor pressure that is extremely low at the operating conditions for its intended use as a dust suppressant, there would be no volatilization into the atmosphere.

Spray application of White Mineral Oil to rough rice at rice handling facilities does not involve use of pneumatic atomization or misting mechanisms. Consequently, the White Mineral Oil will not be subjected to enhanced volatilization (the Kelvin effect), and the quantity and concentration

of White Mineral Oil lost at the use sites to the air environment are expected to be extremely small. See Table 4 for typical vapor pressures of ISO 100 White Mineral Oil as a function of temperature.

Table 4. ISO 100 White Mineral Oil Vapor Pressure

Temperature	Vapor Pressure in mm Hg
@100° F	--
@200° F	--
@300° F	--
@400° F	0.05

Since the effective application rate for dust control of rough rice (800 ppm) is above the level approved for commodity grain under U. S. FDA 21 CFR §172.878, we conducted a field test in order to determine the ultimate fate of White Mineral Oil applied to rough rice for dust control. Experimental evidence from the field test indicates that 12% of the total White Mineral Oil in milled rice fractions ends up on the edible white rice, with 88% remaining on the rice hulls. Please see Exhibit A for a complete set of findings for this test.

Please note that while our initial tests were performed with ISO 46 White Mineral Oil, our conclusions would apply to the use of either ISO 46 or ISO 100 viscosity grade. Our recent Grain Inspection, Packers and Stockyards Administration (GIPSA) sponsored pilot tests, run to determine the effect on quality and milling yield, were performed with ISO 100 (Duoprime Oil RD-H) White Mineral Oil. We found that the ISO 100 White Mineral Oil can be sprayed with the same equipment and at the same nozzle pressure with no increase in electrical power. The tests indicated the same degree of dust control at the 0.08% application level, with no loss of spray efficiency observed.

Since the spraying properties are the same for both the ISO 100 and the ISO 46 White Mineral Oils, the viscosity grade should not significantly alter the distribution of White Mineral Oil in the rice, rice bran, and hulls. And, since 88% of the White Mineral Oil remains with the rice hull, any minor alteration in partitioning among the milled fractions of rough rice would be inconsequential.

Introduction into the Environment via Overspray Loss

Assessment of potential spray loss is important to establish realistic estimates of introduction quantities of White Mineral Oil into the environment. To ascertain the possibility of White Mineral Oil lost to the environment during spray application, the experimental data provided in Exhibits A and B were used to calculate an estimated spray efficiency. The spray efficiency is the ratio of the total quantity of White Mineral Oil recovered from the rough rice (and its milled components) and the total quantity *nominally* applied. We estimate the spray efficiency to be 73%, and the White Mineral Oil spray residue deposited or accumulated at rice handling facilities to be 1707 tons/year. The following calculations were used to obtain the 73% spray efficiency: Based upon our data in Exhibit A, the spray efficiencies for 400 ppm (0.04% by weight), 600 ppm (0.06%), and 800 ppm (0.08%) nominal treatments are 89.3%, 61.0%, and 70.9%, respectively. (For example, at the 400 ppm application rate, the total concentration of White Mineral Oil actually found to be present on the rice components was 357 ppm, which is the sum of 315 ppm for the rice hulls component and 42 ppm for the white rice component. Therefore, the spray efficiency is computed as 357 ppm found/400 ppm applied x 100% = 89.3%. Spray efficiencies for the remaining application rates are similarly computed from the

experimental data.) We calculate from the data in Exhibit B that the spray efficiencies for 600 ppm (0.06%) and 1200 ppm (0.12%) treatments are 73.3% and 68.1%, respectively.

It is important to note that the data from Exhibit A are based upon test samples taken under actual operating conditions at a rice handling facility, and that the data from Exhibit B are based upon test samples from laboratory simulation of rice handling facility conditions. The accuracy of the data from rice handling facility trials is limited by the uncertainty of flow rate of rough rice. The accuracy of data from laboratory simulation trials is limited by the uncertainty of the quantities of White Mineral Oil absorbed to the surface of the tumbling test chamber and spray drift losses, and by the extremely small amounts of oil applied during the experiment. However, we believe that these uncertainties still apply to operating conditions at rice handling facilities. During actual operations there will always be inaccuracy in rough rice flow rate delivery and losses of White Mineral Oil due to surface absorption to walls and rice handling equipment and drift losses of spray.

We believe that the experimental data support the conclusions that the spray efficiency is independent of application rates between 400 and 1200 ppm, both sets of experimental data are consistent even though very different experimental conditions were used, and an average value for the spray efficiency is warranted and effectively acts as a correction factor *that adjusts for uncertainty.* The average spray efficiency for all five tests is 72.5%. Therefore, we expect that, at most, 27% (1707 tons/yr) of the quantity of the initially applied White Mineral Oil (6324 tons/yr) will remain at the rice handling facilities and that, at least 73% (4617 tons/yr) of the applied quantity of White Mineral Oil will actually be retained and quantitatively accounted by the treated rough rice before further processing (6324 tons White Mineral Oil/year x 27 tons spray loss/100 tons applied = 1707 tons White Mineral Oil spray loss at use sites/year).

Introduction into the Environment from Disposal

Disposal into Water via Human Excretion

Because White Mineral Oil is not absorbed during digestion, the oil contained in any rice product used as food will be eliminated as an undigested component of human excreta. Therefore, the estimated quantity of White Mineral Oil that is consumed by humans, eliminated, and discharged into a domestic sewage system would be 554 tons/year. This quantity is based on 12% of the total quantity of White Mineral Oil, 6324 tons, that would have been used to treat entirely the 1991 U.S. rice harvest and a spray efficiency of 73%. (6324 tons White Mineral Oil/year x 73 tons White Mineral Oil retained by rough rice/100 tons White Mineral Oil applied x 12 tons White Mineral Oil partitioned into non-parboiled white rice/100 tons White Mineral Oil retained by rough rice = 554 tons White Mineral Oil in white rice consumed by humans/year.) We calculated that the maximum concentration of White Mineral Oil that could be discharged by Publicly Owned Treatment Works (POTWs) cannot be greater than 0.009 mg/L (ppm). The estimate is based on the statistic that 70% of the U.S. population is served by POTWs[6] the statistic that the total mass of POTW effluent is 4.5×10^{10} tons/year, the experimental evidence that 73% of the White Mineral Oil is retained by rough rice, the experimental evidence that 12% of the retained White Mineral Oil is partitioned into non-parboiled white rice, the assumption that all edible rice is not parboiled, and the assumption that White Mineral Oil is totally soluble in POTW wastewater and is discharged in the POTW effluent (zero mass removal efficiency).

[6]These values were calculated from information reported in U.S. EPA *1992 Needs Survey: Report to Congress,* EPA 832-R-93-002, Washington, DC, September 1993.

(554 tons White Mineral Oil eliminated (entire U.S. population basis)/year x 70 persons served by POTWs/100 persons (entire U.S. population basis) x 1 year/(4.5 x 10^{10}) tons POTW effluent = 0.0086 ppm White Mineral Oil discharge concentration.)

However, in POTWs, White Mineral Oil as a component of domestic sewage will behave like other fats, oils, and greases (FOG) and will separate with the dewatered sewage solids (sludge) for which it has a high affinity. Because White Mineral Oil is insoluble in water and has a high affinity for solids,[7] the actual concentration of White Mineral Oil in POTW discharges to receiving waters is anticipated to be much smaller than the maximum expected concentration, which is based on the absence of any deletion mechanisms. Furthermore, the maximum expected concentration of 0.009 mg/L is wholly devoid of meaning as an analytical parameter because that value is too low to be measured gravimetrically by standard methods of water analysis acceptable to environmental regulatory authorities.

We calculate that the maximum concentration of White Mineral Oil that could be discharged by domestic septic systems into tile fields cannot be greater than 0.050 mg/L (ppm). The estimate is based on the statistics that 30% of the U.S. population is served by septic tank treatment systems,[8] the total mass of septic tank treatment effluent is 3.35 x 10^9 tons/year,[8] the experimental evidence that 73% of the White Mineral Oil is retained by rough rice, the experimental evidence that 12% of the retained White Mineral Oil is partitioned into non-parboiled white rice, the assumption that all edible rice is not parboiled, and the assumption that White Mineral Oil is totally soluble in domestic wastewater and is discharged in the septic tank effluent (zero mass removal efficiency). (554 tons White Mineral Oil eliminated (entire U.S. population basis)/year x 30 persons served by septic systems/100 persons (entire U.S. population basis) x 1 year/(3.35 x 10^9) tons domestic septic system effluent = 0.0496 ppm White Mineral Oil discharge concentration.) However, similar to the analysis for POTWs discussed previously, White Mineral Oil will behave like FOG and will separate in the septic tank with the dewatered sewage solids (sludge). Again, because White Mineral Oil is insoluble in water and has a high affinity for solids, the actual concentration of White Mineral Oil in septic tank discharges to tile fields is anticipated to be much smaller than the maximum expected concentration which is based on the absence of any depletion mechanisms. The magnitude of the maximum expected concentration for White Mineral Oil in septic tank effluents, 0.050 ppm, has no meaningful environmental value because such a magnitude is too low to be measurable by acceptable gravimetric analytical methods.

Entry into Land after Human Excretion

Because of high affinity for solids, White Mineral Oil is expected to separate with sewage sludge. In areas not served by POTWs, human excrement containing White Mineral Oil is discharged into septic treatment systems; however, the sludge will be disposed in the same manner as POTW sewage sludge. We calculate that the maximum concentration of White Mineral Oil that could be separated into digested sewage sludge cannot be greater than 0.00009%. The estimate is based on the statistic that the annual generation rate of POTW digested sewage sludge is 6 x 10^8 tons/year,[9] the insolubility of White Mineral Oil in domestic

---

[7]Mineral oils tend to coat surfaces according to Metcalt and Eddy, Inc., *Wastewater Engineering: Treatment, Disposal, Reuse*, 2nd ed., Edited by George Tchobanoglous, McGraw-Hill, New York, 1979, p.84.

[8] Calculated from information given in Larry W. Canter and Robert C. Knox, Septic Tank System Effects on Ground Water Quality, Lewis Publishers , Inc., Chelsea, MI, 1985, p. 2.

[9] Calculated from information reported in *Federal Register*, 58 (32), 9348-9415 (February 19, 1993), "Standards for the Use or Disposal of Sewage Sludge; Final Rules," p. 9256.

wastewater (100% mass removal efficiency), the evidence of 12% White Mineral Oil in non-parboiled rice, the evidence of 73% spray efficiency, the assumption that all consumed rice is not parboiled, and the assumption that all White Mineral Oil consumed by humans is eliminated to POTWs (554 tons White Mineral Oil eliminated (entire U.S. population basis)/year x 1 year/(6 x 10^8) tons digested sludge (dry basis) x 100% = 0.000092% White Mineral Oil in digested sludge). As noted previously, White Mineral Oil as a component of domestic sewage will behave like FOG. The typical FOG concentration range in digested sewage sludge is about 0.3 to 2.4% by weight.[10] White Mineral Oil in digested sewage sludge is anticipated to be about 3300-fold smaller in concentration than the smallest FOG concentration typically present in digested sludge.

Entry into Atmosphere after Human Excretion

We estimate that the amount of White Mineral Oil that could be incinerated as a component of sewage sludge is 89 tons/year. The estimate is based on the statistic that the proportion of POTW digested sewage sludge that is incinerated is 16.1%,[17] the evidence of 12% White Mineral Oil in non-parboiled white rice, the evidence of 73% spray efficiency, the assumption that all consumed rice is not parboiled, the insolubility of White Mineral Oil in domestic wastewater (100% mass removal efficiency), and the assumption that all White Mineral Oil consumed by humans is eliminated to POTWs. (554 tons White Mineral Oil eliminated (entire U.S. population basis) and became a component of POTW sewage sludge/year x 16.1 tons POTW sewage sludge incinerated/100 tons POTW sewage sludge generated (entire U.S. population basis) = 89.2 tons White Mineral Oil incinerated in POTW digested sewage sludge/year.) [10]

Entry into Land via Animal Excretion

We believe that the use of rice hulls alone has little value as animal feed, in part, because of a high silicon content that is harmful to digestive and respiratory organs.[11] However, rice hulls as a component of rice mill feed can be used to supplement or partly replace other feed for animals. The rice hull content of rice mill feed is nominally about 60%.[12] In 1991, about 584,000 tons of rice mill feed were utilized for commercial animal feed.[13] Consequently, the estimated quantity of rice hulls that could be used, directly without modification, in animal feed is 350,400 tons (60% of 584,000 tons). The disparity is about 4.5-fold between an assumed 100% consumption and the actual consumption of rice hulls used in animal feed in 1991.[14]

---

10 Calculated from data given in Metcalf and Eddy, Inc., *Wastewater Engineering: Treatment, Disposal, Reuse*, 2nd Ed., Edited by George Tchobanoglous, McGraw-Hill, New York, 1979, Table 11-4, p. 583, and in Syed R. Qasim, *Wastewater Treatment Plants: Planning, Design, and Operation*, Technomic, Lancaster, PA 1994, Table 16.1, p. 428.

11 A.D. Tillman, R.D. Furr, K.R. Hansen, L.B. Sherrod, and J.D. Wood, Jr., *J. Animal Sci.*, **29**, 792-796 (1967), "Utilization of rice hulls in cattle finishing rations." and A. Margaritis, G.Rowe, and T.Baltus, *Dev. Ind. Microbiol.*, 21, 305-311 (1980), "Enzymatic hydrolysis of rice hulls."

12 B. Harris, Jr., and C.R. Staples, *Energy and Milling By-Product Feedstuffs of Dairy Cattle*, Fact Sheet DS 36, Florida Cooperative Extension Service, University of Florida, August 1991.

13 Table 69 on page I-45 of United States Department of Agriculture, Agricultural Statistics 1996-86, U.S. Government Printing Office, Washington DC lists 584,000 tons of rice mill feed disappearance for commercial utilization as animal feed in 1991. For rice mill feed with a nominal composition of 60% rice hulls, the quantity of rice hulls utilized for commercial animal feed in 1991 is calculated as 584,000 tons mill feed x 60 tons rice hulls/100 tons mill feed = 350,400 tons rice hulls.

14 A minimum 4.5-fold difference still persists between assumed total use of rice hulls as animal feed and actual use of rice hulls in animal feed even when more recent 1994 agricultural statistics are evaluated assuming a maximum 60% rice hull content for rice mill feed by-product.

We estimate that the maximum amount of White Mineral Oil that could enter the environment as a consequence of animal excretion is 902 tons/year (1991 basis). This quantity is based on conclusions derived from experimental evidence that 88% of the White Mineral Oil applied to non-parboiled rough rice stays with the rice hulls after milling and the spray efficiency for White Mineral Oil as a rice dust suppressant is 73%. The computed quantity also relies on the estimate that about 22% of milled rice hulls is used for animal feed. (6324 tons White Mineral Oil applied as a dust suppressant/yr x 73 tons White Mineral Oil retained on rough rice/100 tons White Mineral Oil applied x 88 tons White Mineral Oil partitioned into rice hulls/100 tons White Mineral Oil retained on rough rice x 22.2 tons rice hulls used as animal feed/100 tons rice hulls milled = 902 tons White Mineral Oil consumed and excreted by animals/year.)

If animal excreta were completely gathered and entirely managed as manure for agricultural fertilization of cropland, then the White Mineral Oil content from animal feed would become incorporated in surface land. The estimated usable amount of manure produced by confined animals in the U.S. is at least 61 million tons/yr. [15]

In general, animal manure as a fertilizer should be applied to fields at a rate compatible with the nutrient needs of the crop being grown. Determining the rate at which manure nutrients should be applied requires consideration of crop requirements and nutrients already present in the soil. The rate of manure application may range between 2 to 20 tons/acre and usually would not exceed 25 tons/acre.[16] Incorporation of the manure into a soil of bulk density of 83 lbs/ft^3 by tilling to a depth of 0.5 ft would result in a soil concentration of White Mineral Oil of about 0.4 ppm at the maximum rate of manure application of 25 tons/acre (902 tons White Mineral Oil in manure/year x 1 year/(61 x 10^6) tons manure x 125 tons manure applied/acre x 1 acre/43560 ft^2 x 1/0.5 ft soil depth x 1 ft^3 soil/83 lbs soil x 2000 lbs/ton = 0.409 ppm White Mineral Oil incorporated into soil.)

The estimate additionally depends on assuming no deletion mechanisms for the White Mineral Oil, assuming an unusual maximum rate of manure application to tilled agricultural land, and using the Environmental Protection Agency's (EPA) assumptions of average values of 15 centimeters (0.5 ft) soil depth and 1.33 grams per cubic centimeter (83 lbs/ft^3) soil bulk density for a soil incorporation model.[17]

Entry into the Atmosphere from Rice Hull Incineration

We believe that incineration probably would account for a significant portion of White Mineral Oil disposal if the proposed action were approved. We estimate that approximately 34% of rice hulls are burned for heating and power requirements in the U.S. We summarize our analysis of known information as follows: A significant use of rice hulls is to provide heat and electrical energy at areas in or contiguous with the rice farming regions of the six major rice-growing states of the U.S. One source estimates that at least 5% of rough rice (25% of rice hulls) is burned as

---

15 Council for Agricultural Science and Technology (CAST) News Release, *Animal Wastes a Growing Environmental Issue*, Council for Agricultural Science and Technology, 4420 West Lincoln Way, Ames, IA 50014-3447, November 5, 1996 and CAST, *Integrated Animal Waste Management*, Report 128, Ames, IA, November 1996.

16 Fred Madison, Keith Kelling, Jim Petersen, Tommy Daniel, Gary Jackson and Leonard Massie, *Managing Manure and Waste: Guidelines for Applying Manure to Pasture and Cropland in Wisconsin*, University of Wisconsin Extension Service, November 1986 and Elbert C. Dickey and Gerald R. Bodman, *Fertilization of Crops with Feedlot Manure* Beef Cattle Handbook GPE-7601, Cooperative Extension Service Great Plains States.

17 *Federal Register*, **58**(32), 9248-9415 (February 19, 1993), "Standards for the Use or Disposal of Sewage Sludge; Final Rules," Table I-2, p. 9257.

fuel.[18] The statistic represents the disposition of rice harvests in the states of Arkansas, Louisiana, Texas, and Mississippi.

Therefore, the statistic neglects any rice hull fuel contribution from the rice-growing states of California and Missouri. Missouri's rice harvests are small so that any combustion of a portion of the state's rice harvest may be neglected. However, California's rice harvest is about 22% of the national harvest, and a substantial portion of the harvest's rice hulls are burned so that California's rice hull fuel contribution cannot be neglected. The Floyd Myers Marsh Power Plant, operated by Wadham Energy for Pacific Gas and Electric, in Williams, CA is reported to use two-thirds of California's annual rice hull production.[19]

Consequently, we estimate that about 34% of rice hulls are used as fuel in the U.S. (25% rice hulls used as fuel in four rice-growing states x 78 tons rice harvest in the same four states (neglecting Missouri's contribution)/100 tons rice harvest in U.S. + 67% rice hulls used as fuel in California x 22 tons rice harvest in California/100 tons rice harvest in U.S. = 34.2% U.S. use of rice hulls as fuel).

The quantity of White Mineral Oil that would become incinerated as a consequence of using rice hulls as a fuel is about 1389 tons/year. The estimate is based on the assumption that all U.S. rice production is subject to the proposed use of White Mineral Oil as a dust suppressant at an application rate of 800 ppm, evidence of a 73% spray efficiency, evidence that 88% of the oil partitions into rice hulls, and an estimate that about 34% of the U.S. rice hulls are burned. (6324 tons White Mineral Oil required to treat entirely the 1991 rice harvest/year x 73 tons White Mineral Oil retained by rough rice/100 tons White Mineral Oil applied x 88 tons White Mineral Oil partitioned into non-parboiled rice hulls/1090 tons White Mineral Oil retained by rough rice x 34.2 tons rice hulls used as fuel/100 tons non-parboiled rice hulls milled = 1389 tons White Mineral Oil incinerated with rice hulls used as fuel/year.)

Upon incineration, the fate of White Mineral Oil is conversion to carbon dioxide, water, and ash. From our analysis, we estimate that the amount of White Mineral Oil that could be incinerated as a component of sewage sludge is 89 tons/year and the amount that becomes incinerated as a consequence of using rice hulls as a fuel is 1389 tons/year. We anticipate that about 1478 tons/year of White Mineral Oil will be incinerated, altogether.

The quantity of carbon dioxide produced from incineration of 1478 tons/year of White Mineral Oil would be about 4590 tons CO_2/year. (1478 tons White Mineral Oil incinerated/year x 1 ton-mole White Mineral Oil/425 tons White Mineral Oil x 30 ton-mole C/1 ton-mole White Mineral Oil x 1 ton-mole CO_2/1 ton-mole C x 44 tons CO_2/1 ton-mole CO_2 = 4590 tons CO_2 incinerator emissions from White Mineral Oil decomposition/year.) The computation depends on the molecular weights of White Mineral Oil (Table 1 of the petitioner's EA) and carbon dioxide and the mole ratio for 100% decomposition of White Mineral Oil into carbon dioxide.

---

[18] Walter W. Rose, Leo D. Pedersen, Harold Redsun, and R. Scott Butner, *Significance of Food Processing By-Products as Contributors to Animal Feeds*. Phase I. Food Processing Survey, U.S. EPA, Office of Pesticide Programs, Washington, DC, Contract Number: 68-02-4263, EPA/HED #08, October 1989.

[19] Neos Corporation, *California Biomass Facilities Directory Survey Report*, California Energy Commission and U.S. Dept. of Energy, Western Regional Biomass Energy Program, Contract DE-AC65-90WA65637, Task 5, March 28, 1991.

The quantity of carbon dioxide emissions from combustion of White Mineral Oil in rice hulls and sewage sludge would be about 0.0002% of the U.S. carbon dioxide emissions from all petroleum products.[20] Therefore, combustion products from White Mineral Oil incineration will not add significantly to the emissions of incinerators and are expected not to affect the terrestrial and atmospheric environments.

Entry into Atmosphere via Landfill Disposal of Rice Processing Residues

The EPA sponsored survey, Significance of Food Processing By-Products as Contributors to Animal Feeds, Phase I, Food Processing Survey, provides the statistic that 1% of the rough rice harvest becomes processing waste that is disposed in landfills. Applying that statistic to rice hulls as the principal disposable milling wastes, we estimate that about 41 tons of White Mineral Oil/year would be disposed in landfills, if the proposed action were approved, (6324 tons White Mineral Oil required to treat entirely the 1991 rough rice harvest/year x 73 tons White Mineral Oil retained by rough rice/100 tons White Mineral Oil applied x 88 tons White Mineral Oil partitioned into non-parboiled rice hulls/100 tons White Mineral Oil retained by rough rice x 1 ton rice harvest disposed in landfills/100 tons non-parboiled rice harvest milled = 40.6 tons White Mineral Oil partitioned into non-parboiled rice hulls disposed in landfills/year.)

Entry into Atmosphere via Unknown Routes from Unaccounted Uses

A sum of 3473 tons of White Mineral Oil cannot be allocated to a specific disposal from use. Survey errors or unknown disposal practices for POTW sludge account for 35 tons/year.[21] About 1731 tons of White Mineral Oil in rice hulls cannot be reconciled. (6324 tons White Mineral Oil required to treat entirely the 1991 rough rice harvest/year x 73 tons White Mineral Oil retained by rough rice/100 tons White Mineral Oil applied x 88 tons White Mineral Oil partitioned into non-parboiled rice hulls/100 tons White Mineral Oil retained by rough rice x 42.6 tons rice hulls of unknown use and disposal/100 tons rice hulls milled = 1731 tons White Mineral Oil in rice hulls of unknown use and disposal/year).[22] Other possible uses of rice hulls for which White Mineral Oil disposal cannot be accounted for include use as packing materials, industrial abrasive aids, fertilizer manufacture, and the manufacture of industrial chemical derivatives. The quantities for possible overspray residue accumulation (1707 tons/year) on structural surfaces of the rice handling facilities and on-site accumulation of rice hulls (1731 tons/year) together constitute over one-half the total environmental introduction of White Mineral Oil. Public information about disposal routes is incomplete or unavailable and the relevance of evaluating impacts on the human environment is directly related to a low probability for occurrence of impacts. Due to the low volatility of White Mineral Oil and its insolubility in water, environmental exposures to this chemical will be limited, and, therefore, significant impacts on

---

[20] Calculated from data in U.S. EPA, Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-1993, EPA 230-R-94-014, Office of Policy, Planning, and Evaluation, Washington DC, September 1994, p. ES-5. In 1990, the U.S. emitted 1,335 million metric tons of carbon equivalent from fossil fuel combustion. Petroleum products accounted for about 44% of total U.S. energy-related carbon dioxide emissions. (4590 tons carbon dioxide from combustion of White Mineral Oil considered as a petroleum fossil fuel/year x 1 year/1,335,000,000 metric ton x C emitted from fossil fuels x 100 metric tons fossil fuel/44 metric tons petroleum used as fuel x 1 metric ton/1.1 tons x 12 tons C/44 tons carbon dioxide x 100% = 0.000194%.)

[21] The calculated estimate for POTW sludge is based on the statistic that disposal of 6.3% of POTW sludge cannot be established. The statistic is taken from the Federal Register, **58**(32), 9248-9415 (February 19, 1993), "Standards for the Use or Disposal of Sewage Sludge; Final Rules," p. 9257. The statistic is applied to the 554 tons/year of White Mineral Oil consumed by humans, eliminated, and separated in POTWs as treated sewage sludge.

[22] On the basis of the analysis, 34.2% of all rice hulls are used as fuel, 22.2% of all rice hulls are used as animal feed from mill feed by-product, and 1% of all rice hulls are assumed to be disposed in landfills. The remaining unaccounted use or disposal of the rice hull milled fraction of rough rice is 42.6% which is the difference between 100% and the sum of accounted uses and disposal.

the environmental effects from introductions of any unaccounted quantities of White Mineral Oil are unlikely.

7. Fate of White Mineral Oil in the Environment:

Air--As previously mentioned in section 6, the fate of White Mineral Oil in the atmosphere (due to loss at use sites) is limited by its very low volatility. Therefore, emissions of White Mineral Oil into air are expected to be extremely small, if any emissions occur at all, as a consequence of the proposed action. Upon incineration, the fate of White Mineral Oil is conversion to carbon dioxide, water, and ash. The quantity of carbon dioxide produced from incineration of 1478 tons/year is about 4590 tons CO2/year based on the following calculation: (1478 tons White Mineral Oil incinerated/year x 1 ton-mole White Mineral Oil/425 tons White Mineral Oil x 30 ton-mole C/1 ton-mole White Mineral Oil x 1 ton-mole CO2/1 ton-mole C x 44 tons CO2/1 ton-mole CO2 incinerator emissions from White Mineral Oil decomposition/year). Again, the quantity of carbon dioxide emissions from combustion of White Mineral Oil in rice hulls and sewage sludge would be about 0.0002% of the U.S. carbon dioxide emissions from all petroleum products. Therefore, combustion products from White Mineral Oil incineration will not add significantly to the emissions of incinerators and are not expected to affect the terrestrial and atmospheric environments.

Land--Although long-term studies are not available regarding the biodegradability of White Mineral Oil, evidence is available to substantiate a 60% decomposition rate into carbon dioxide and water within 50 days.[23] In addition, the amount of carbon dioxide produced from the biodegradation of White Mineral Oil in the environment due to this application will be minuscule. Attachment C (referenced in footnote 23) provides an overview of biodegradation of and environmental effects created by lubricants.

Biodegradability of materials can be divided into three categories: *readily* biodegradable, *ultimately* biodegradable, and *non* biodegradable (recalcitrant). Ultimate biodegradation is the complete degradation of a chemical or substance to yield carbon dioxide, water and inorganic substances. The primary difference between readily biodegradable and ultimately biodegradable materials is time--the rate of biodegradation. Biodegradability studies are usually performed over a specified time period, during which time the microbes are in contact with the test material. Readily biodegradable materials are those which degrade to an appreciable extent (usually 60-70% or more) in standard tests, usually in 21 or 28 days. Ultimately biodegradable materials will biodegrade, but do not meet the time requirements for classification as "readily biodegradable". While vegetable oil, a readily biodegradable material, may be 60% biodegraded within 28 days, a White Mineral Oil will only reach 60% within 50 days in the standard tests currently used. White Mineral Oil is ultimately biodegradable, when given additional time.

Water--In the absence of depletion mechanisms, for all applicable use and disposal sites, the fate of White Mineral Oil in the aquatic ecosystem is limited by its insolubility in water and its very high affinity for solids, and, therefore, the concentration of White Mineral Oil in receiving waters is expected to be extremely small, if measurable at all.

8. Environmental Effects of Released Substances:

[23]Bruce A. Narloch Ph.D., *Exposing the Myths of Vegetable-Based Lubricants*, Chevron Lubricants 1993 Jobber Sales Conference, Chevron Research and Technology Company, December 4, 1993.

Based on the analysis of the introductions and fate of White Mineral Oil, we do not expect that the proposed action will threaten the environment, nor be in violation of relevant laws and regulations for protecting the environment.

Air-- Atmospheric emissions are not possible at the normal storage temperatures for White Mineral Oil. The quantity of carbon dioxide emissions from combustion of White Mineral Oil in rice hulls and sewage sludge would be about 0.0002% of the U.S. carbon dioxide emissions from all petroleum products. Therefore, combustion products from White Mineral Oil incineration will not add significantly to incinerator emissions and are not expected to affect the terrestrial and atmospheric environments.

Further, the estimated maximum amount of combustion products entering the atmosphere due to the proposed action (1478 tons/yr) would seem a desirable alternative to the present dust particle emissions at rice handling facilities, estimated to be between 8,695 tons/yr and 43,447 tons/yr. Based on a 1987 Texas A & M study conducted on corn and milo, dust concentrations in grain range from 0.11% to 0.55% by weight, and at an application rate of 200 ppm, corn retains approximately 83.8% of the available dust, and milo retains 73.7%.[24] We estimate the rice dust capture from the use of White Mineral Oil at an application rate of 800 ppm to be at least 78.7% (average of 83.8% and 73.7%). Assuming the same dust concentration for rice as for other grains, and based on the 1991 rice crop, the amount of rice dust generated would be between 8,695 tons/yr (15,810,000,000 lb divided by 2,000 lbs/ton times 0.11%) and 43,447 tons/yr (15,810,000,000 lb divided by 2,000 lbs/ton times 0.55%).

Land--The effects of disposal in municipal landfills of White Mineral Oil as a component of substances affected by the proposed action are controlled by environmental regulations. EPA's regulations require new municipal solid waste landfill units and lateral expansions of existing units to have composite liners and leachate collection systems to prevent leachate from entering ground and surface water and to have groundwater monitoring systems (40 CFR Part 258). Although owners and operators of existing active municipal solid waste landfills that were constructed before October 9, 1993, are not required to retrofit liners and leachate collection systems, they are required to monitor groundwater and to take corrective action as appropriate. The effects of White Mineral Oil as a component of sewage sludge that is surface disposed or used for soil amendment are adequately controlled by environmental regulations. Management practices for surface disposal and land application of sewage sludge are regulated under 40 CFR 505 to protect threatened or endangered species, wetlands, surface water and groundwater. For surface disposal sites with liners, the leachate must be collected by a leachate collection system and be disposed in accordance with applicable requirements. If leachate is discharged to surface waters, then an NPDES permit is required. For surface disposal sites that do not have leachate collection systems, the runoff must be collected and disposed in accordance with applicable requirements to ensure that runoff (which may contain pollutants) is not released into the environment. Land application of sewage sludge is regulated similarly, which includes management practices to prevent the introduction of pollutants from sewage sludge into the environment.

---

24 Wardlaw, Parnell, Lesikar, *Dust Suppression Results With Mineral Oil Applications for Corn and Milo*, ASAE Paper #87-6550, pages 1 & 7.

Although no ecological toxicity data on White Mineral Oil are available, from numerous published chronic studies involving various rodent species, the International Agency for Research on Cancer has concluded that there is no evidence of carcinogenicity to laboratory animals from White Mineral Oils. These studies concerned repeated application to their skin or incorporation into their normal diets. This confirms the many years of safe medical and pharmacological use of these products. In fact, a large majority of toxicity experiments with laboratory animals use White Mineral Oils with the same chemical properties and compositions as our Duoprime Oils as "blind" negative controls.[25]

In addition, the potential impact of White Mineral Oil has been evaluated in limited studies. Acute studies were performed by the Utah Biomedical Test Laboratory in 1989, on the ARCOprime Oils 70 and 400. (ARCOprime Oils were renamed Duoprime Oils in 1992, due to a change in company ownership. The products tested in 1989 are now called Duoprime Oil 70 (ISO 13) and Duoprime Oil 400 (ISO 78). Duoprime Oils 70 and 400 are the same material as Duoprime Oil RD-H (ISO 100) White Mineral Oil, but with a lower molecular weight. Results applicable to the product family were as follows:

Study Title	ARCOprime Oil 70	ARCOprime Oil 400
Acute Oral Toxicity	LD50>5.0 g/kg	LD50>5.0 g/kg
Acute Dermal Toxicity	LD50>2.0 g/kg	LD50>2.0 g/kg
Primary Dermal Irritation	Non-irritating	Non-irritating
Primary Eye Irritation	Non-irritating	Non-irritating
Skin Sensitization	Negative	Negative
Acute Inhalation Toxicity	LC50>5.0 mg/L	LC50>4.5 mg/L

Water-- Any trace amount of White Mineral Oil permeating from landfill to sub-surface water or otherwise introduced to land surface water, prior to its biodegradation, would not produce deleterious matter in the water, nor adversely affect water quality, since White Mineral Oil is not miscible with water. Water solubility in White Mineral Oil is typically less than 50 ppm water. The effects of exposure to White Mineral Oil in the aquatic environment receiving POTW discharges to surface water or septic tank discharges to groundwater are anticipated to be extremely limited because White Mineral Oil is insoluble in water and has a high affinity for solids. Regulatory activities for the protection of groundwater quality by state and municipal authorities limit the environmental impact of septic tank treatment systems. Wastewater discharges of oils from POTWs also are limited by environmental permit, issued by state or municipal authorities, under effluent standards mandated by the NPDES which protects the quality of surface water.

---

25 International Agency for Research on Cancer, *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Polynuclear Aromatic Hydrocarbons, Part 2, Carbon Blacks, Mineral Oils (Lubricant Base Oils and Derived Products) and Some Nitroarenes,* Vol. 33, World Health Organization, Lyon, 1984, pp. 87-168.

9. Use of Natural Resources and Energy:

Natural Resources

Based upon our analysis, a maximum of 6324 tons of White Mineral Oil would be required annually for rice dust application in the U.S. Current White Mineral Oil production will handle demands for rice handling facilities for the foreseeable future. Therefore, we expect no increase in oil reserve demand as a result of the proposed action. Because mineral oil has been in production for a long period of time, no additional lands will be needed to produce it.

Energy

In contrast to other grain handling facilities, rice handling facilities have never needed to control dust emissions because rice dust is not conducive to explosion or fire. Therefore, most rice handling facilities have no dust control system in place today. In order to reduce the amount of dust they emit, and comply with Federal Clean Air Act Amendments of 1990, there are two commercial technologies available to rice handlers: 1) conventional pneumatic technology uses an air circulating system which moves and deposits grain dust onto massive filters or in a spiral-shaped collection vessel, and 2) the more recent oil spray method, which controls dust by adherence of dust particles to the oiled surface of the grain via surface tension.

Pneumatic technologies use enormous amounts of electricity, and are too expensive for most rice handling facilities to operate. The energy required by current (pneumatic) methods for removing dust from dusty air may exceed the energy required to move the grain.[26] When compared to the alternative pneumatic dust control technology, oil spray systems use 0.17% the electrical energy to operate. A pneumatic system at a grain handling facility is typically driven by a 100 horse power (hp) motor, requiring 75 kW/hr to operate. In contrast, typical oil spray systems are driven by a one-sixth hp (0.17 hp) motor[27], which requires only 0.13 kW/hour to operate (0.746 kW/hp times 0.17 hp/hr = 0.13 kW/hr), or 0.17% of pneumatic bag filter systems). Further, there is sufficiency of present ISO 100 White Mineral Oil production by U.S. White Mineral Oil producers to meet the anticipated quantity needed for rice dust control. No additional energy will be needed to produce it.

10. Effect on Endangered/Threatened Species and National Historical Sites:

National historical sites will not be affected/corroded by the decomposition of White Mineral Oil into the atmosphere. No adverse Endangered/Threatened Species or National Historical Sites impacts are associated with the proposed action; therefore, no mitigation measures are necessary.

11. Alternatives to the Proposed Action:

Because there are no potential adverse environmental impacts due to this proposed action, we conclude that no alternative to the proposed action is necessary.

---

[26] F. S. Lai, Associate Member ASAE, B. Miller, C. Martin, C. Story, L. Bolte, M. Shogren, K.F. Kinney, and J.K. Quinlan, "Reducing Grain Dust with Oil Additives", *Trans. ASAE*, 24, 1626-1631 (1981).

[27] Al Emfinger, Owner, STE Oil (and Pump) Supply, P. O. Box 1033, San Marcus,Texas 78667

12. List of Preparers:

John M. Noreyko - Manager, Technical Services and Training, Lyondell Lubricants, LYONDELL-CITGO Refining Company Ltd. Area of expertise (34 years) in White Mineral Oil, lubricants, waxes and petrochemicals, their manufacture, properties and applications, as well as governmental regulations.

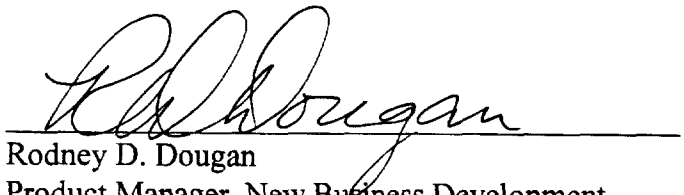
Rodney D. Dougan - Product Manager, New Business Development, Lyondell Lubricants, LYONDELL-CITGO Refining Company Ltd. Area of expertise (12 years) in White Mineral Oil and lubricants, their manufacture, properties and applications as well as governmental regulations.

Melinda A. White - Environmental Engineer Intern, Health, Safety & Environmental, Lyondell-CITGO Refining Company Ltd.

13. Certification:

The undersigned official certifies that the information presented is true, accurate, and complete to the best of the knowledge of the firm or agency responsible for preparation of the environmental assessment.

April 2, 1998



Rodney D. Dougan
Product Manager, New Business Development
LYONDELL-CITGO Refining Company Ltd.

APPENDICES

- Attachment A:
  Test Procedure for the Determination of White Mineral Oil on Edible "White" Rice

- Attachment B:
  Test Procedure for the Determination of White Mineral Oil on Edible White Rice During the Parboil Process

- Attachment C:
  Exposing the Myths of Vegetable-Based Lubricants

- Attachment D:
  Biodegradability - Review of the Current Situation

ATTACHMENT "A"

Preamble: Test procedure for the determination of White Mineral Oil on edible "white" rice

Testing was conducted to ascertain the degree of penetration of White Mineral Oil through the protective rice hull. White Mineral Oil was applied to rough rice using a commercial spray applicator. The spray system was set for White Mineral Oil application rates of 400 ppm, 600 ppm and 800 ppm.

Application rate calibration is dependent on the volume of rough rice delivered by the screw conveyor during a given time period. For the test, rice flow was controlled by a worker manually pulling open a "gate" above the screw conveyor. This allowed the amount of rough rice delivered to be measured at only an approximate flow rate, which turned out to be slightly higher than estimated.

As a result, only about 360 ppm of White Mineral Oil was accounted for on the 400 and 600 ppm (nominal) treated rice and 570 ppm on the 800 ppm (nominal) treated rice.

17

NATIONAL INSTITUTE FOR PETROLEUM AND ENERGY RESEARCH
Post Office Box 2128
Bartlesville, Oklahoma 74005
(918) 336-2400

SINCE 1936

April 5, 1993

Mr. Rodney D. Dougan
Product Manager
Lyondell Petrochemical Company
Houston Refinery
12000 Lawndale
P.O. Box 2451
Houston, TX 77252-2451

Dear Mr. Dougan:

As requested, we have analyzed the various rice, hull, and grain samples you provided for determination of the degree of penetration of the dust abatement white oil into the rice grains. A copy of a report of the results obtained is enclosed.

The analyses indicated about 12% of the total white oil detected ended up on the hulled rice grains, with the remainder on the hulls.

If you have any questions regarding the report or wish to discuss any additional work, please give us a call; Gene at (918) 337-4314, Jim at (918) 337-4312. We appreciate this opportunity to be of service.

Sincerely,

Gene P. Sturm, Jr.

Gene P. Sturm, Jr.
Manager, Fuels Chemistry Research
Department of Fuels Research

James W. Reynolds
Research Chemist
Fuels Chemist Research

Enclosure

cc w/encl:
John Noreyko

EXPERIMENTS TO DETERMINE OIL PENETRATION IN RICE TREATED WITH DUOPRIME 200 WHITE OIL

SUMMARY:

In order to ascertain the degree of penetration of dust abatement oil into rice grains, samples of whole brown rice were treated with increasing levels of oil. After dehulling, the hulls and corresponding hulled rice were analyzed by Soxhlet extraction and High Performance Liquid Chromatography (HPLC). Analysis of the concentrated extracts showed almost all detectable white oil to be concentrated in the hulls, with very low concentrations of oil in the hulled rice, indicating that the oil does not significantly penetrate the hulls on treatment.

EXPERIMENTAL:

Samples of treated rice hulls and hulled rice, along with their untreated counterparts and untreated rice bran were received in polyethylene zipper locking plastic bags. Treated products had been treated at three nominal levels of oil; 400 ppm, 600 ppm and 800 ppm.

Each product was extracted in duplicate with approximately 800 mL of HPLC/Pesticide grade *n*-pentane for 2 hours by Soxhlet extraction as follows:

- The clean, dry apparatus was assembled, and the fiber cups were pre-extracted with pentane for two hours. The cups were then dried at 60° C for one hour, cooled for an hour in a dessicator and weighed.

- The product to be extracted was placed into the extraction apparatus and extracted for 2 hours with approximately 800 mL of pentane. Extraction solvent was removed by rotary evaporation and the concentrates stripped to constant weight in tared vials at 60° C and 20 inches Hg vacuum.

An initial attempt to determine oil by gas chromatography resulted in too many problems with overlapping retention times and incomplete resolution of natural oils with the paraffinic DUOPRIME 200 oil, so GC analysis was abandoned in favor of HPLC.

The extracts were dissolved in *n*-hexane to a volume of 5.00 mL. Diluted extracts were run by HPLC on a Waters Associates HPLC using a WISP 712 sample processor for injection and run time control. Detection was accomplished using a differential refractive index detector (RI)

at attenuation of 16X and 8X. The column used for the analysis was prepared from Merck LiChrosorb Si-60 (10 um) silica gel (activated overnight at 150 ° C) and slurry packed at 12,000 psi into a 25 cm X 4.6 mm ID stainless steel column.

Analysis on this column proved to be convenient, since the natural oils were completely adsorbed by the column under the conditions used, producing only a peak for the white oil. Injection volumes of 10 uL were used with a flowrate of 1.5 mL/min and total run time of 25 minutes. Standards of oil in hexane of 1.11, 2.05, 6.04, 9.99, 12.04 and 14.04 mg/mL, respectively, were used to quantify oil concentrations. Hulled rice oil contents were determined directly, while the oil content of the rice hulls had to be calculated on a whole rice basis.

Response factors for each set of runs (in units of mg oil/mL/unit peak height) were calculated by averaging responses of the standards. These factors were used to determine the total oil content of each extract. Determination of oil concentration on treated rice hulls required that it be done on the basis of the whole rice. The mass ratio used was determined by weighing the rice hulls and dehulled rice-which is the total mass of whole rice charged to the hulling machine-and using the ratio of hulls to this total for calculation of white oil content. This is necessary, since the mass of the hulls is only ~21% of the mass of the whole (unhulled) grain, and nearly all of the oil was deposited on the exterior (hull) of the grain. The hulled rice masses were used without consideration of the mass of removed hulls, since the actual concentration of white oil left on hulless grain is the criterion which is set by government standards.

Data: Extraction of untreated rice components

Untreated Whole Rice	Untreated Milled Hulled Rice	Untreated Bran from Milled Rice	Untreated Rice Hulls
Mass Extracted - 70.8880 g	65.2900 g	5.5552 g	45.1462 g
Extract Recovered - 0.0564 g	0.4547 g	1.0748 g	0.3122 g
% extract - 0.08%	0.70	19.35	0.69%

CONCLUSIONS:

Liquid chromatographic analysis of the pentane extracts from rice treated with white dust abatement oil proved to be efficient and reproducible within the range of concentrations required for the determination of the penetration of oil into the rice grain. Natural oils were adsorbed on the column, eliminating the complication of differentiating them from the white oil, which was encountered in an initial attempt to utilize gas chromatography for the analysis. Analysis of the extracts from the treated rice hulls and corresponding dehulled rice show only about 12% of the total oil detected ending up on the hulled rice, with the balance remaining on the hulls. This held true of all levels of treatment (400, 600 and 800 ppm, nominally) and would suggest the possibility that oil on the hulled grain may come more from the dehulling operation than from hull penetration. The amount of oil found on the hulls was consistent between the 8X and 16X refractive index attenuations, but the 16X range did not provide the sensitivity for detection of oil on the dehulled rice grains. Due to the limited amount of sample concentrate and the volatile nature of the hexane solvent, second runs were not attempted because a noticeable fraction of the samples had evaporated overnight from the punctured sample vials and volumetric flasks.

The data showed no significant increase in oil concentration on the hulled rice grains with increase in treatment level from 400 to 600 ppm (nominal) and only a slight increase from 600 to 800 ppm (nominal). It should be noted that about 360 ppm of the white oil was accounted for in the 400 and 600 ppm (nominal) treated rice and 570 ppm in the 800 ppm (nominal) rice.

Extraction of treated rice hulls

	"400 ppm"		"600 ppm"		800 ppm	
	(1)	(2)	(1)	(2)	(1)	(2)
Mass Extracted	20.51 g	20.67 g	19.64 g	24.06 g	16.43 g	18.26 g
Extract Recovered	0.2925 g	0.1953 g	0.0981 g	0.1274 g	0.1083 g	0.1016 g
% Extract	1.43%	0.94%	0.50%	0.53%	0.66%	0.56%
Total Mass (Rice + Hulls)	1568.91 g		1,576.75 g		1,604.85 g	

Extraction of treated hulled rice

	"400 ppm"		"600 ppm"		800 ppm	
	(1)	(2)	(1)	(2)	(1)	(2)
Mass Extracted	97.76 g	103.31 g	96.6564 g	99.7515 g	90.1558 g	96.8692 g
Extract Recovered	0.8212 g	0.6392 g	0.4216 g	0.5744 g	0.3962 g	0.4944 g
% Extract	0.84%	0.62%	0.44%	0.58%	0.44%	0.51%

Rice Hulls	Extracted total mass Run		Ratio of hulls to whole rice Run		Oil peak ht./response factor (mg/mL oil) Run		PPM oil (whole rice basis) Run	
	(1)[a]	(2)[b]	(1)[a]	(2)[b]	(1)[a]	(2)[b]	(1)[a]	(2)[b]
"400 ppm"	20.5064 g	20.67 g	0.222	0.222	15.5/0.369	28.5/0.206	310	315
"600 ppm"	19.6401 g	24.06 g	0.224	0.224	18.2/0.369	33.4/0.206	383	320
"800 ppm"	16.4310 g	18.26 g	0.208	0.208	18.2/0.369	42.6/0.206	425	500
Rice								
"400 ppm"	97.76 g	103.31 g	NA	NA	0/.369	4.2/0.206	nd[c]	42
"600 ppm"	96.66 g	99.75 g	NA	NA	0/.369	4.5/0.206	nd[c]	46
"800 ppm"	90.16 g	96.87 g	NA	NA	0/.369	6.3/0.206	nd[c]	67

[a] Run @ 16X RI.
[b] Run @ 8X RI.
[c] Not detected.

2425 Holly Hall #123
Houston, Texas 77054
Telephone (713) 797 9401

Rodney D. Dougan
Manager
Western Area
White Oil Business Unit

Lyondell Petrochemical Company

January 26, 1993

Mr. Gene Sturm
NIPER
P. O. Box 2128
Bartlesville, OK 74005

Re: Mineral Oil Disposition When Sprayed on Brown Rice

Gene,

In reference to your recent phone conversation with John Noreyko, from Lyondell's Product Technology group, we would like for NIPER to analyze the enclosed rice samples to determine the amount of mineral oil (by weight) that:

1) IS FOUND ON THE RICE KERNEL
2) IS LEFT IN THE HULL
3) IS LEFT IN THE BRAN and/or
4) IS UNACCOUNTED FOR

at three different mineral oil treat levels of 400, 600, & 800 PPM.

Enclosed are:

11 samples submitted in 9 containers

UNTREATED RICE (GALLON CONTAINER)
400 PPM RICE "
600 PPM RICE "
800 PPM RICE "

UNTREATED HULLS (GALLON CONTAINER)
400 PPM HULLS "
600 PPM HULLS "
800 PPM HULLS "

UNTREATED INITIAL SAMPLE/RICE IN HULLS (GALLON CONTAINER)
UNTREATED MILLED RICE (PINT CONTAINER/SHIPPED INSIDE GAL CONTAINER)
UNTREATED BRAN (PINT CONTAINER/SHIPPED INSIDE GAL CONTAINER)

Thank you. Please call Noreyko or myself for any questions you may have regarding this project.

Rodney D. Dougan

RDD/po
wp\wpdoc\niper01.rdd

ATTACHMENT "B"

Preamble: Test procedure for the determination of White Mineral Oil on edible "white" rice during the parboil process

Testing was conducted to determine the degree of penetration of White Mineral Oil through the protective rice hull during the parboil process. The White Mineral Oil was applied using a 25 ml DeVilbis atomizer, calibrated to apply White Mineral Oil to the rough rice at application rates of 600 ppm and 1200 ppm.

Only about 440 ppm White Mineral Oil was accounted for in the 600 ppm treated rice and 817 ppm in the 1200 ppm treated rice. The balance is assumed to have remained on the inside surface of the portable cement mixer used to tumble the rough rice, and exaggerated by the minute quantity of White Mineral Oil used for each test lot (less than 10 ml at 600 ppm application rate, and less than 20 ml at 1200 ppm application rate).

"B"

October 8, 1993

To: Rod Dogan
Lyondell Lubricants

From: Robert R. Cogburn
USDA/ARS

Subject: Application of Mineral Oil to Rough Rice

Dear Rod:

The following is a report of the treatment schedule and experimental design of our cooperative research to assess the fate of mineral oil applied to rough rice for dust control.

A homogeneous lot of 1993 crop long grain 'Gulfmont' rough rice was obtained from the foundation seed program at the Texas A&M Rice Research Center at Beaumont. The rice was passed through a seed cleaner to remove chaff, straw and light kernels and then split into nine samples of 30 pounds each. These samples were placed in new galvanized steel garbage cans which were thoroughly washed with soap and water, rinsed and dried for 24 hours before use.

The intended dosages were 600 and 1200 ppm. Calculations to apply these amounts were:

30 lbs. = 13,620 grams = 13.62 kg

1 ppm = 13.62 mg per 30 lb. sample

600 ppm = 13.62 mg x 600 = 8172 mg = 8.172 grams

Specific gravity of Duoprime DS-H = 0.856 g / ml

600 ppm = 8.172 / 0.856 = 9.546 ml per 30 lb. rice

1200 ppm = 9.456 x 2 = 19.1 ml per 30 lb rice

The rice was treated in a portable cement mixer. A sample of Duoprime DS-H mineral oil was supplied by Rod Dugan. Measured amounts of oil were transferred with a 25-ml pipet to a DeVilbis atomizer which was used to apply the oil to the rice. The atomizer was cleaned for several hours in a heated ultrasonic glassware cleaner with the cleaning solution recommended by the manufacturer, thoroughly rinsed and completely dried before use. Several samples of oil were run through the atomizer to determine the optimum pressure and to estimate the amount of oil that adhered to the glass reservoir. The oil tended to atomize into very fine droplets. The mist vaguely resembled smoke and, when released into the air, would drift in a slight breeze. Also, some of the oil adhered to the reservoir. To compensate for this, 9.55 ml of oil was run through the atomizer immediately

before it was used to treat rice and the atomizer was not cleaned of oil between treatments.

The optimum pressure was determined to be the least amount that would deliver the oil through the instrument. This turned out to be 10-15 psi and this pressure was used for all treatments. To avoid loss of oil from drifting, a circular shield was constructed from cardboard, covered with aluminum foil, and taped to the mouth of the cement mixer after each sample of rice was loaded. The oil was applied through a two-inch hole in the center of the shield while the rice was being tumbled in the mixer. After the oil was applied, the hole was sealed with tape and the rice tumbled for an additional 10 minutes, after which it was stored in the metal containers in the warehouse under ambient conditions.

A very small amount of oil escaped as mist through the two-inch hole in the shield. In my opinion, this amount was negligible - well within the inherent error of the measuring and delivery systems. However, a larger amount of oil adhered to the inner surface of the cement mixer not in contact with the rice. There was no way to measure this. My best guess is a few tenths (0.1-0.3) of a milliliter. I estimate that at least 95% of the intended dosage was applied to the rice. Before the cement mixer was used for any oil treatments, the controls were each tumbled for 10 minutes with no treatment.

Treatment, sampling and processing schedules are as follows:

Oct. 4, 1993--Tumble controls
Oct. 5, 1993--Treat Reps 1&2 600 ppm
Oct. 6, 1993--Treat Rep 3 of 600 ppm and Rep 1 of 1200 ppm
Oct. 7, 1993--Treat Reps 2&3 of 1200 ppm

Oct. 18&19, 1993--Parboil controls; Mill raw controls; Collect raw milling fractions and parboiling water. Take one sample from each Rep of raw rice to FGIS for grading.
Oct. 20, 1993--Mill Reps 1&2 of raw 600 ppm; collect milling fractions; Parboil Reps 1&2 600 ppm; collect water.
Oct. 21, 1993--Mill Rep 3 of 600 ppm and Rep 1 of 1200 ppm raw rice; Parboil Rep 3 600 ppm and Rep 1 1200 ppm; Collect raw milling fractions and parboiling water.
Oct. 22, 1993--Mill Reps 2&3 of 1200 ppm; Parboil Reps 2&3 of 1200 ppm; Collect raw milling fractions and parboiling water.
Oct. 25-29, 1993--Mill all parboiled rice, collect milling fractions and send for chemical analyses.

Analyses to be conducted on this rice are:
Chromatographic analysis of oil in raw rough rice, hulls from parboiled rice, parboiled brown rice and parboiled milled rice.

A sample from each rep will be subjected to the official grading procedure by the Federal Grain Inspection Service.

Entomological Bioassays--Test insects will be rice weevils, lesser grain borers, Angoumois grain moths and red flour beetles.

No-Choice Tests--Four 50-gram samples from each rep of each treatment will be placed in glass pint jars with filter paper covers. Fifty 2-week old adults of the beetle species will be added to a jar from each rep. These will be observed for mortality after 1, 2 and 3 weeks exposure. Surviving adults will be removed and the F1 generation will be recorded as it emerges. For Angoumois grain moths, 100 eggs will be added to the samples and emergent adults will be counted and recorded.

Free-Choice Tests--Four 100-gram samples from each rep will be secured in insect-permeable bags and randomly distributed in an infestation chamber. One thousand of each of the test species will be released in the chamber and allowed equal access to all samples. An additional 1000 of each species will be released two weeks later. One sample from each rep will be collected after exposures of 1, 2, 3 and four weeks. Adult insects will be counted and removed from the samples. F1 progeny will be counted and recorded as they emerge. When all F1s have emerged, the samples will be re-weighed to determine weight loss.

Milling Yield--Standard procedures will be used to determine the total and whole-grain milling yield for each treatment.

Cereal Chemistry--Standard procedures will be used to determine:

Amylose Content
Free Fatty Acids
Gelatinization Temperature
Gel Viscosity

Rod, all of this probably tells you more than you want to know but I wrote it as much for myself and Bill Webb as for you guys. It provides us with a well defined experimental plan which should help us avoid violation of the eleventh commandment--"Thou shalt not screw up".

Sincerely,

Bob

Robert A. Cogburn

Determination of White Oil Content of Oil-Treated Parboiled Rice Products

Summary

Twenty-seven samples of rice components were analyzed for white oil content by solvent extraction and subsequent High Performance Liquid Chromatography. The white oil content of the final food product obtained from the parboiling/milling operation (the milled, parboiled rice) was 9.3 - 11.5 ppm for the grain treated at a nominal 600 ppm rate and 17.7-19.5 ppm for the grain treated at a nominal rate of 1200 ppm (w/w).

Experimental

Extraction of sample and preparation for HPLC analysis.

The twenty-seven samples consisted of rice and parboiling/milling by-products described below. These samples were received in sealed, one quart Mason canning jars.

Table 1. - Sample Number and Description

Sample Number	Description
CK-1 Rough Raw	Untreated Whole rice
CK-2 Rough Raw	Untreated Whole rice
CK-3 Rough Raw	Untreated Whole rice
600-1 Rough Raw	Whole Rice-Treated @ 600 ppm, nominal, white oil (Duoprime 200)
600-2 Rough Raw	Whole Rice-Treated @ 600 ppm, nominal, white oil (Duoprime 200)
600-3 Rough Raw	Whole Rice-Treated @ 600 ppm, nominal, white oil (Duoprime 200)
600-1 Rough Parboiled	Unmilled, parboiled 600-1
600-2 Rough Parboiled	Unmilled, parboiled 600-2
600-3 Rough Parboiled	Unmilled, parboiled 600-3
600-1Hulls, Parboiled	Hulls milled from 600-1 Rough Parboiled
600-2Hulls, Parboiled	Hulls milled from 600-2 Rough Parboiled
600-3Hulls, Parboiled	Hulls milled from 600-3 Rough Parboiled
600-1 Milled Parboiled	Finished Rice from milling 600-1 Rough Parboiled
600-2 Milled Parboiled	Finished Rice from milling 600-2 Rough Parboiled
600-3 Milled Parboiled	Finished Rice from milling 600-3 Rough Parboiled
1200-1 Rough Raw	Whole rice treated with 1200 ppm nominal, white oil (Duoprime 200)
1200-2 Rough Raw	Whole rice treated with 1200 ppm nominal, white oil (Duoprime 200)
1200-3 Rough Raw	Whole rice treated with 1200 ppm nominal, white oil (Duoprime 200)
1200-1 Rough Parboiled	Unmilled, parboiled 1200-1 Rough Raw
1200-2 Rough Parboiled	Unmilled, parboiled 1200-2 Rough Raw
1200-3 Rough Parboiled	Unmilled, parboiled 1200-3 Rough Raw
1200-1 Hulls, parboiled	Hulls from parboiled 1200-1 Rough Raw
1200-2 Hulls, parboiled	Hulls from parboiled 1200-2 Rough Raw
1200-3 Hulls, Parboiled	Hulls from parboiled 1200-3 Rough Raw
1200-1 Milled, Parboiled	Finished rice from milling 1200-1 rough parboiled
1200-2 Milled, Parboiled	Finished rice from milling 1200-2 rough parboiled
1200-3 Milled, Parboiled	Finished rice from milling 1200-3 rough parboiled

Extraction and HPLC sample preparation:

Each of the samples was extracted in a soxhlet extractor for 2 hours with 800 mL of HPLC grade pentane (EM product number PX0167-1, EM Industries Inc., Gibbstown, NJ 08027). The samples were held in fiber cups, which were pre-extracted in pentane and dried to constant weight. The pentane extract was reduced in volume by a clean rotary evaporator and the concentrate was quantitatively transferred to 5 mL volumetric flasks and the volumes adjusted to 5 mL in n-Hexane. The extracts contained some insoluble matter, but this settled quickly to the bottom and did not interfere with the subsequent HPLC analysis.

High-Performance Liquid Chromatographic Analysis of Extract Concentrates.

The prepared samples were transferred to 4 mL sample vials with Teflon-backed silicone rubber septa caps. Chromatographic analysis was done using a system consisting of a Rheodyne 7120 Sample Injector with a 20µL sample loop, a Waters, Inc., 6000 A HPLC pump, and a 4.6mm x 20cm stainless steel column packed with LiChrosorb Si-60 10µ silica which was activated at 150° C/24 hours. A hexane mobile phase of 2.0 mL/minute was used with 20µL injection volumes of all samples and standards; detection was accomplished with a Waters, Inc., Model R401 differential refractometer and a Linear Model 585 strip-chart recorder. Attenuations of 16X and 32X were used, depending on the concentration of oil as witnessed by peak heights.

The standards of Lyondell Duoprime 200 oil in n-hexane were made up in concentrations of:

1 - $2.10X10^{-2}$ g/mL - named Standard 1, but not used
2 - $1.01X10^{-2}$ g/mL - named Standard 2
3 - $1.10X10^{-3}$ g/mL - named Standard 3, but not used
4 - $6X10^{-4}$ g/mL - named Standard 4
5 - $1X10^{-4}$ g/mL - named Standard 5

Standards were run in triplicate and the average peak height used for quantitation.

The oil extracts were made up in 5.00 mL of n-Hexane as described above. All sample and standard injection volumes were 20µL, with adjustment of Refractive Index attenuation to give peaks of at least 1/3 of the chart width for the more concentrated oil samples. Multiplication of the average peak heights in Table 2 by five times the response factor yields the total mass of oil in the extract.

Example:

From Table 2, sample 600-3MP gives a response of 2.5 units @ 16X. Standard number 5 gives an average response of 1.0 units. The response factor for standard 5 (concentration of 0.0001 g of oil per milliliter) is 0.0001 g/mL/1 unit or $1X10^{-4}$ g/mL/unit peak height for Duoprime oil. The actual mass of oil in the 5.00 mL extract concentrate is obtained by multiplying its average peak height by the response factor and multiplying this product by 5 mL in the total extract:

2.5 units X $1X10^{-4}$ g/mL/unit peak ht. X 5mL = 0.00125 g of oil.
Dividing this by the sample weight extracted (108.52 g) gives a final concentration of $1.15X10^{-5}$ or 11.5 parts per million oil in the extracted sample.

Table 2. - Sample/Analysis Data

Sample #	Average 20µL* Peak Height at Attenuation( )	Standard /Peak Number/Height	Response Factor g/mL/Unit Peak Ht.	Original Total Oil In Sample, g	Sample Weight, g	Oil, PPM
CK-1	2.5(16X)	5/1.0	$1.00X10^{-4}$	$1.25X10^{-3}$	84.28	15.0
CK-2	2.1(16X)	5/1.0	$1.00X10^{-4}$	$1.05X10^{-3}$	85.45	12.4
CK-3	2.0(16X)	5/1.0	$1.00X10^{-4}$	$1.00X10^{-3}$	87.62	11.4
600-1RR	42.5(32X)	2/55.2	$1.83X10^{-4}$	$3.86X10^{-2}$	89.42	435
600-2RR	43.4(32X)	2/55.2	$1.83X10^{-4}$	$3.97X10^{-2}$	86.65	458
600-3RR	41.2(32X)	2/55.2	$1.83X10^{-4}$	$3.77X10^{-2}$	88.31	427
600-1RP	15.6(32X)	2/55.2	$1.83X10^{-4}$	$1.43X10^{-2}$	75.56	189
600-2RP	35.8(32X)	2/55.2	$1.83X10^{-4}$	$3.27X10^{-2}$	71.10	460
600-3RP	32.7(32X)	2/55.2	$1.83X10^{-4}$	$2.99X10^{-2}$	70.19	426
600-1MP	2.4(16X)	5/1.0	$1.00X10^{-4}$	$1.20X10^{-3}$	112.35	10.7
600-2MP	2.0(16X)	5/1.0	$1.00X10^{-4}$	$1.00X10^{-3}$	107.82	9.3
600-3MP	2.5(16X)	5/1.0	$1.00X10^{-4}$	$1.25X10^{-3}$	108.52	11.5
600-1HP	36.7(32X)	2/55.2	$1.8X10^{-4}$	$3.36X10^{-2}$	19.98	1681
600-2HP	35.2(32X)	2/55.2	$1.8X10^{-4}$	$3.22X10^{-2}$	17.92	1797
600-3HP	37.2(32X)	2/55.2	$1.8X10^{-4}$	$3.40X10^{-2}$	22.19	1532
1200-1RR	76.6(32X)	2/57.8	$1.75X10^{-4}$	$6.70X10^{-2}$	83.90	799
1200-2RR	81.4(32X)	2/57.8	$1.75X10^{-4}$	$7.12X10^{-2}$	85.26	835
1200-3RR	76.5(32X)	2/57.8	$1.75X10^{-4}$	$6.69X10^{-2}$	81.77	818
1200-1RP	58.3(32X)	2/53.6	$1.88X10^{-4}$	$5.48X10^{-2}$	67.47	812
1200-2RP	67.9(32X)	2/53.6	$1.88X10^{-4}$	$6.38X10^{-2}$	72.42	881
1200-3RP	70.8(32X)	2/53.6	$1.88X10^{-4}$	$6.65X10^{-2}$	76.10	874
1200-1MP	3.3(16X)	4/5.0	$1.20X10^{-4}$	$1.98X10^{-3}$	111.87	17.7
1200-2MP	3.5(16X)	4/5.0	$1.20X10^{-4}$	$2.10X10^{-3}$	107.51	19.5
1200-3MP	3.5(16X)	4/5.0	$1.20X10^{-4}$	$2.10X10^{-3}$	110.18	19.1
1200-1HP	20.8(32X)	2/57.8	$1.75X10^{-4}$	$1.82X10^{-2}$	19.42	937
1200-2HP	80.8(32X)	2/57.8	$1.75X10^{-4}$	$7.07X10^{-2}$	18.65	3791
1200-3HP	86.7(32X)	2/57.8	$1.75X10^{-4}$	$7.59X10^{-2}$	21.95	3458

CK = Check Sample RR = Rough, Raw RP = Rough Parboiled MP = Milled Parboiled HP = Parboiled Hulls

* All HPLC Injections are 20µL.

Conclusions

From the data obtained in this work, it appears that by far the majority of the oil absorbs into the hull portion of the grain, even after parboiling. The concentration of oil detected on the treated rough raw and rough parboiled grains are both high, but not to the theoretical level. The milled rice after parboiling retains very little of the oil and appears to show an increase in oil content roughly proportional to the treat level.

Data obtained on the hulls after parboiling cannot be interpreted unless the ratio of hull to grain is known. As a casual observation, however, it would appear that the hulls retain by far the bulk of the treat oil, since the milled grain is very low in oil content.

MES
Mercury Environmental Services
(713) 920-2502
1604 South Shaver • Pasadena, Texas 77502

November 09, 1993

Lyondell Lubricants
P.O. Box 2451
Houston, TX 77252-2451

ATTENTION: Mr. Rodney D. Dougan

SAMPLE NUMBERS: 311011 - 311037

SAMPLE I.D.:

Sample #01 / 0-1-E	Sample #15 / 600-3-L
Sample #02 / 0-2-E	Sample #16 / 600-1-S
Sample #03 / 0-3-E	Sample #17 / 600-2-S
Sample #04 / 0-1-L	Sample #18 / 600-3-S
Sample #05 / 0-2-L	Sample #19 / 1200-1-E
Sample #06 / 0-3-L	Sample #20 / 1200-2-E
Sample #07 / 0-1-S	Sample #21 / 1200-3-E
Sample #08 / 0-2-S	Sample #22 / 1200-1-L
Sample #09 / 0-3-S	Sample #23 / 1200-2-L
Sample #10 / 600-1-E	Sample #24 / 1200-3-L
Sample #11 / 600-2-E	Sample #25 / 1200-1-S
Sample #12 / 600-3-E	Sample #26 / 1200-2-S
Sample #13 / 600-1-L	Sample #27 / 1200-3-S
Sample #14 / 600-2-L	

DATE RECEIVED: November 02, 1993

CERTIFICATE OF ANALYSIS

MES NUMBERS	SAMPLE I.D.	TOTAL RECOVERABLE OIL & GREASE 413.1	MDL mg/L	RESULTS mg/L	DATE/TIME/ANALYST
311011	#01 / 0-1-E		1	< 1	11-02-93 0900 MAG
311012	#02 / 0-2-E		1	< 1	
311013	#03 / 0-3-E		1	< 1	
311014	#04 / 0-1-L		1	< 1	
311015	#05 / 0-2-L		1	< 1	
311016	#06 / 0-3-L		1	< 1	
311017	#07 / 0-1-S		1	< 1	
311018	#08 / 0-2-S		1	< 1	11-03-93 1400 BTC
311019	#09 / 0-3-S		1	< 1	
311020	#10 / 600-1-E		1	< 1	11-04-93 1830 MAG
311021	#11 / 600-2-E		1	< 1	
311022	#12 / 600-3-E		1	< 1	

CERTIFICATE OF ANALYSIS CONTINUED

MES NUMBERS	SAMPLE I.D.	TOTAL RECOVERABLE OIL & GREASE 413.1	MDL mg/L	RESULTS mg/L	DATE/TIME/ANALYST
311023	#13 /	600-1-L	1	< 1	11-04-93 1830 MAG
311024	#14 /	600-2-L	1	< 1	
311025	#15 /	600-3-L	1	< 1	
311026	#16 /	600-1-S	1	8	
311027	#17 /	600-2-S	1	5	
311028	#18 /	600-3-S	1	4	
311029	#19 /	1200-1-E	1	< 1	11-07-93 1300 HWA
311030	#20 /	1200-2-E	1	< 1	11-08-93 0830 HWA
311031	#21 /	1200-3-E	1	< 1	
311032	#22 /	1200-1-L	1	< 1	11-08-93 1100 HWA
311033	#23 /	1200-2-L	1	< 1	
311034	#24 /	1200-3-L	1	4	11-08-93 1430 HWA
311035	#25 /	1200-1-S	1	4	
311036	#26 /	1200-2-S	1	5	11-08-93 1815 HWA
311037	#27 /	1200-3-S	1	4	

Signature: _____ Date: 11-09-93
Howard W. Apel II / Laboratory Manager

Signature: _____ Date: 11-09-93
Holland D. Gilmore / Laboratory Director

311011 - 311037

QUALITY ASSURANCE

METHOD EPA 413.1

ANALYTE	MB mg/L	LCS % REC
Total Recoverable Oil & Grease	< 1	82.1

Signature: Billie J. Jacobs

Billie J. Jacobs / QA-QC Officer

Date: 11-09-93

USDA Parboiling Test

September, 1993

USDA to treat rough rice @ 3 levels, 3 reps each, mill to 4 component parts, then package & store

Rough	Hulls	Brown	Bran	Milled	Water	Steam
0	0	0	0	0	0	0
600	600	600	600	600	600	600
1200	1200	1200	1200	1200	1200	1200

*3 components to be analyzed by NIPER

Rough	Hulls	Milled
0	0	0
600	600	600
1200	1200	1200

2 components stored by USDA for analysis by NIPER if necessary

Brown	Bran
0	0
600	600
1200	1200

*Parboil water to be collected by USDA & analyzed locally

Water
0
600
1200

*3 rice components, 3 reps @ 3 treat levels = 27 analyses @ NIPER
*water sample, 3 reps @ 3 treat levels = 9 analyses @ local lab

Costs of the Bagfilter System

Capital cost to install 100 hp bagfilter

Estimated project cost to install new bagfilter	**$ 200,000.00**
Estimated project cost to install used bagfilter	**$ 150,000.00**

Operating costs for 100 hp bagfilter

Electrical costs

	kW/hp	hp/hr	kW/hr
hp to kW/hr	0.746	100	74.6

	$/kW	kW/hr	$/hr
kW/hr to $/hr	0.05	74.6	$ 3.73

	hrs/yr	$/hr	$/yr
yearly operating cost	8,000	$ 3.73	*$ 29,840.00*

Maintenance costs

	# of bags	$/yr/bag	$/yr
Cost to replace bags	250	$ 9.00	$ 2,250.00

	manhours	$/hr	$/yr
Labor - repairs	384	$ 15.00	$ 5,760.00

	cfm	hp used	$/yr
Compressed air usage	50	12.5	$ 4,562.50

Total maintenance costs *$ 12,572.50*

Total estimated operating costs	**$ 42,412.50**

Riceland Foods, Inc.
Stuttgart Rice Division

Daniel Lafayette
12/10/97

ATTACHMENT C

EXPOSING THE MYTHS OF VEGETABLE-BASED LUBRICANTS

Bruce A. Narloch Ph.D.
Chevron Research and Technology Company

Chevron Lubricants 1993 Jobber Sales Conference

Saturday, December 4, 1993

Introduction

Industry has responded to public environmental concerns over the past few years in both its operating procedures and the products it produces. Not the least affected are industries which utilize or manufacture lubricants. In some countries, such as Germany, the government has adopted regulations that place strict requirements on the toxicity and environmental impact of lubricants and fluids used in environmentally sensitive applications. In the United States the criteria used to define "environmental" lubricants and hydraulic fluids have been largely developed by the manufacturers of alternative products themselves, rather than by regulatory agencies.

As a result of mis-information and conflicting claims, significant confusion has arisen regarding what constitutes an "environmental" lubricant or hydraulic fluid. Many questions exist concerning issues such as biodegradation, toxicity, environmental fate and waste requirements for lubricants. Furthermore, the facts concerning the legal requirements for reporting and managing leaks or spills of these products, and for disposing of used materials, have often been mis-represented. The following paper is an attempt to unravel the 'myths' that have been generated surrounding 'environmental' lubricants and fluids, and to clarify these issues.

Biodegradation

Biodegradation is generally defined as the metabolic breakdown of a chemical or substance by microbial organisms. It is usually measured in a controlled aqueous (water) or solid (soil) medium containing an inoculum of aerobic sewage sludge (as a source of microbes). These tests are usually performed over the course of 21 or 28 days, during which the microbes are in contact with the test material. There are two general categories of biodegradation, either 'primary' or 'ultimate' biodegradation.

'Ultimate biodegradation' is the complete degradation of a chemical or substance to yield carbon dioxide, water and inorganic substances. Ultimate biodegradation is usually evaluated indirectly, by measuring 'demand for oxygen' or 'carbon dioxide evolution.' Of the test methods commonly used to evaluate biodegradability (Appendix I), the Modified Sturm Test (OECD 301 B) is perhaps the most widely used.

'Primary biodegradation' is the breakdown of a chemical or substance to produce a new chemical or substance. This conversion can be as simple as the removal of one carbon atom from the original chemical or substance, and does not generally give an indication of the ability of the material to completely biodegrade. A common test method used to measure primary biodegradation is the CEC-L-33-T-82 test.

Biodegradability is usually described as the rate (or percentage) of biodegradation over time. There are three terms which are generally used to describe the relative biodegradability of materials: readily biodegradable, inherently biodegradable, and recalcitrant (non-biodegradable).

'Readily Biodegradable' materials are those that degrade to an appreciable extent (usually 60 - 70% or more) in standard tests within a specified time period (often 21 or 28 days). Most vegetable oils, many synthetic esters, and some polyalphaolefins meet this definition.

'Inherently biodegradable' materials will biodegrade, but do not meet the time requirements for classification as 'readily biodegradable'. In the standard tests currently used, most mineral oils and many mineral oil-based lubricants fall into this category. However, these materials are often ultimately biodegradable when given additional time.

Recalcitrant materials are resistant to biodegradation. Examples of recalcitrant materials include many inorganic chemicals, extremely water-insoluble organic chemicals, most plastics, glass and aluminum.

The primary factor separating materials which may be defined as 'readily biodegradable' from those which are inherently biodegradable' is time. 'Figure 1' (Appendix 2) compares biodegradation rates in the Modified Sturm Test for both typical vegetable oil and the mineral oil used in Chevron's new ashless hydraulic oil. While the vegetable oil is 60% biodegraded within 28 days, and can therefore be considered 'readily biodegradable,' Chevron's mineral oil is biodegraded and attains the 60% level within 50 days. Whether a material requires 28 days or 50 days to appreciably biodegrade may not be of major significance in a real environmental spill situation. Under similar circumstances, both materials are expected to biodegrade. The common misconception that vegetable-oil based lubricants will biodegrade in the environment while mineral oil-based lubricants will not is entirely false.

Toxicity

There is a natural tendency to believe that anything derived from nature is inherently less toxic than that which is man-made. This misconception carries over to most people's understanding of the relative toxicity of products which are vegetable-oil based and those which contain mineral oils. The fact is that both vegetable-derived and mineral-derived oils are extracted (or Distilled) from natural substances, and are further refined and modifies to meet the requirements of a lubricating base oil. It is the chemistry of the final refined oil which determines its toxicity.

Although a number of different toxicology indices must be evaluated to determine a chemical or substance's overall toxicity, the acute aquatic toxicity (LC-50) test is frequently used to describe a material's potential environmental impact. If the acute aquatic LC-50 for a substance is greater than 1,000 mg/liter (ppm), the material is generally considered to be 'non-toxic' for aquatic organisms. Marketers of vegetable oil-based lubricants frequently cite acute aquatic toxicity test results for their products in excess of 1,000 mg/liter. Chevron has performed acute aquatic toxicitytesting on its new ashless hydraulic oil and demonstrated that the acute LC-50 for this product in rainbow trout is in excess of 1,000 mg/liter. Again, the perception that lubricants based on refined vegetable oils are inherently less toxic than those containing mineral oils is incorrect.

Leaks, Spills and Liability Concerns

Leaks or spills of any oil-based material into the environment requires attention, whether it is vegetable oil or mineral oil-based. A common claim made by manufacturers of vegetable oil-based lubricants is that, because these materials are considered biodegradable and non-toxic, leaks or spills of these materials are of little concern. The biodegradation and aquatic toxicity data for Chevron's new ashless hydraulic oil indicate that it, too, should not present a significant environmental hazard in the case of small leaks or spills. Chevron is currently petitioning the California Department of Toxic Substances Control (CA DTSC) for confirmation that its new ashless hydraulic oil is a non-hazardous waste.

Regardless of whether an oil product is classified as hazardous or non-hazardous, there are separate federal and state laws governing the clean-up of oil spills which must be complied with. Spills of all oils to marine waters, whether vegetable or mineral based, must be reported to the National Response Center. Most state and local agencies evaluate spills or leaks to soil based on the TCLP (Toxicity Characteristics Leachate Procedure), and the Oil and Grease soil extraction test (EPA 413.1, 413.2, and 418.1). The results of the TCLP are used to test for the presence of toxic metals and other priority pollutants. The Oil and Grease test is used to evaluate the presence of oil-derived hydrocarbons. Regulatory agencies typically evaluate the results of these tests to determine the extent of contamination and degree of hazard associated with a contaminated site. Ultimately, an appropriate state or local regulatory agency has the responsibility of determining whether oil-contaminated soil or water is subject to clean-up, and the appropriate levels of clean-up.

Waste Disposal and Recycling Issues

Chevron believes that its new ashless hydraulic oil meets California DTSC requirements as a non-hazardous material. However, once a lubricant (whether vegetable based or mineral based) is in service, hazard classification must be evaluated based on the used material. This is due to potential contamination of the oil during use with metals or other toxic substances. The disposal requirements for vegetable oil-based lubricants are the same as those for mineral oil-based lubricants. It is the responsibility of the generator of a waste to evaluate the status of the material prior to disposal.

In the case of mineral oil-based lubricants, extensive oil recycling programs have been established. It is widely recognized that mineral oils represent a valuable resource which should be conserved. As a result, commercial facilities capable of re-refining used mineral oils have been constructed. These facilities currently pick-up used mineral oil-based lubricants and transform them into 'new' lubricant base oils. Because of this extensive recycling effort, mineral oils have an almost endless potential life. They can be repeatedly reclaimed, re-refined and re-used as lubricant base oils. No similar recycling processes are currently in place for vegetable oil-based lubricants because these materials are poor starting materials for current re-refining technology. Vegetable oil-based products have a finite life, and the used material is only suitable for burning as a waste or fuel.

Performance Comparisons

Certain physical and chemical characteristics inherent to vegetable oils limit their applications and usefulness in today's performance-demanding, high-technology equipment. The use of vegetable oils as lubricants is not a recent phenomenon. During the industrial revolution, vegetable oils were used as lubricants before petroleum-derived oils became widely available. Once mineral oils became readily available, however, they replaced vegetable oils due to their superior performance, longer life and versatility. During World War II, when the Japanese were cut off from petroleum supplies, they were forced to rely upon vegetable oils to lubricate their industrial and military machinery. Equipment failures resulting from the use of vegetable oils as lubricants during this period were common-place and well documented. More recently, several lubricant manufacturers have introduced vegetable based hydraulic oils as environmental lubricants. An examination of several important performance properties essential to these fluids suggests that even newer vegetable-based hydraulic fluids may have problems in meeting equipment manufacturers' requirements, and in performing under typical use conditions.

Oxidation Stability

Oxidation occurs when an oil is heated in the presence of air. As the oil oxidizes, both its viscosity and the concentration of organic acids increase. These increases can cause varnish and deposit formation on metal surfaces, resulting in increased maintenance and shortened equipment life. The rate of oxidation is accelerated by the presence of water and wear metals.

There are currently two standard test methods for determining the oxidation stability of hydraulic fluids that are approved by the American Society for Test Methods (ASTM). These test methods are the Turbine Oil Stability Test (TOST), and the Rotating Bomb Oxidation Test (RBOT). Vegetable oil-based hydraulic fluids behave poorly in both of these oxidation tests when compared to their mineral oil counterparts. The reported TOST life of a commercial vegetable hydraulic oil is less than 75 hours, compared to typical TOST lives of 1500 to 7000 hours for mineral oil-based hydraulic fluids. Similarly, vegetable oil-based hydraulic oils typically yield RBOT results of 25 minutes or less, compared to 200 to 500 minutes for mineral oil-based lubricants.

Water Contamination

Under normal conditions of storage or use, hydraulic oils may become contaminated with water to varying degrees. Hydraulic fluids must be able to withstand water contamination without degradation or loss of performance. Mineral oils may be contaminated with significant amounts of water without appreciable loss of performance. Two factors inherent to vegetable oils predispose vegetable oil-based fluids to performance loss from water contamination.

Hydrolytic instability is a primary concern with the use of vegetable oil-based lubricants. Hydrolysis is the chemical cleavage of a molecule by water into two or more fragments. Materials, such as vegetable oils, which contain hydrolyzable chemical bonds are subject to attack by water contamination. This attack leads to breakdown of vegetable oil molecules into smaller fragments which, depending upon the extent of contamination, may significantly decrease hydraulic fluid performance and result in the deposition of additives. Mineral oils have chemical compositions that are significantly more resistant to hydrolysis than those of vegetable oils.

Susceptibility to microbial degradation is another factor which increases the sensitivity of vegetable oils to water contamination. Water serves as both a means for bacterial to invade a hydraulic fluid as well as a medium for them to survive in while they gradually degrade the oil. While mineral oils are biodegradable, they are much less sensitive to small levels of microbial contamination than are vegetable oils. Microbial degradation of vegetable based hydraulic fluids may result in hydraulic oil color changes and odor problems, as well as loss of fluid performance.

Viscosity Characteristics

The selection of appropriate viscosity fluids for different hydraulic applications is critical. The viscosity chosen is dependent upon the operating temperature of the system. The use of an oil with a viscosity lower than required may lead to fluid leakage and excessive equipment wear. Alternately, the use of an oil with a viscosity higher than required may result in pump cavitation, lower system control response, and reduced system efficiency.

Modern petroleum refining techniques allow for the separation and purification of petroleum into mineral oils of varying viscosity. Hence, mineral oil-based hydraulic fluids are available in a wide range of viscosities, from which the appropriate viscosity fluid can be selected for a specific application. Because of their more uniform chemical composition, vegetable oils are generally available in only one viscosity grade, 36 cSt at 40°C. With a viscosity index of approximately 205, these oils resemble an ISO 46 viscosity grade at most operating temperatures. Thus, those applications requiring either an ISO 32 or ISO 68 grade will sacrifice some level of performance or protection in order to use a vegetable hydraulic fluid.

Low Temperature Performance

For mineral-based lubricants and hydraulic fluids, the low temperature solidification point is referred to as the "pour point". When ambient temperature drops below the pour point for a mineral-based hydraulic fluid, it tends to solidify and its pourability and performance is significantly compromised. For vegetable-based hydraulic fluids, the solidification point is often much higher than the reported pour point. In discussing low temperature performance for vegetable-based fluids, therefore, "solidification point" is a more meaningful term than pour point. The pour point for mineral-based hydraulic fluids is generally in the range of -27°F, while the solidification point for ~~mineral~~ vegetable-based fluids is approximately 42°F. At temperatures below 50°F, vegetable based fluids may become cloudy and begin to solidify. For mobile equipment that has been left idle for a period of time in cold weather, start-up with a semi-solid hydraulic system would experience low efficiency, and may result in equipment failure.

Fluid Compatibility

All hydraulic fluids must be replaced at intervals as performance decreases, and wear metals and contaminants accumulate. Furthermore, fluid losses commonly occur which require "make-up" oil to be added to the system. Fluid compatibility allows fluid changes or additions to be made with fluid which is available or appropriate for the system's operation at the time. The compounding used in some mineral oil-based fluids may be incompatible with vegetable oil-based fluids, due to the increased sensitivity of vegetable oils to chemical degradation. Therefore, "make-up" of vegetable oil-based systems with mineral-based fluids should not be performed without complete knowledge of fluid compatibility. Alternately, for optimal performance and fluid life, switching from a mineral oil-based fluid to a vegetable oil-based fluid should only be performed after thorough flushing of the system. Where fluid compatibility is a concern, mineral oil-based fluids offer a distinct advantage over their vegetable oil-based counterparts.

Conclusion

Recent concerns over the potential impacts of industries operating in environmentally sensitive areas have not gone unheeded. In the past several years, the world marketplace has been flooded with a number of products aimed at minimizing man's impact upon the environment. Among the many new "environmental" products recently marketed are lubricants and hydraulic fluids.

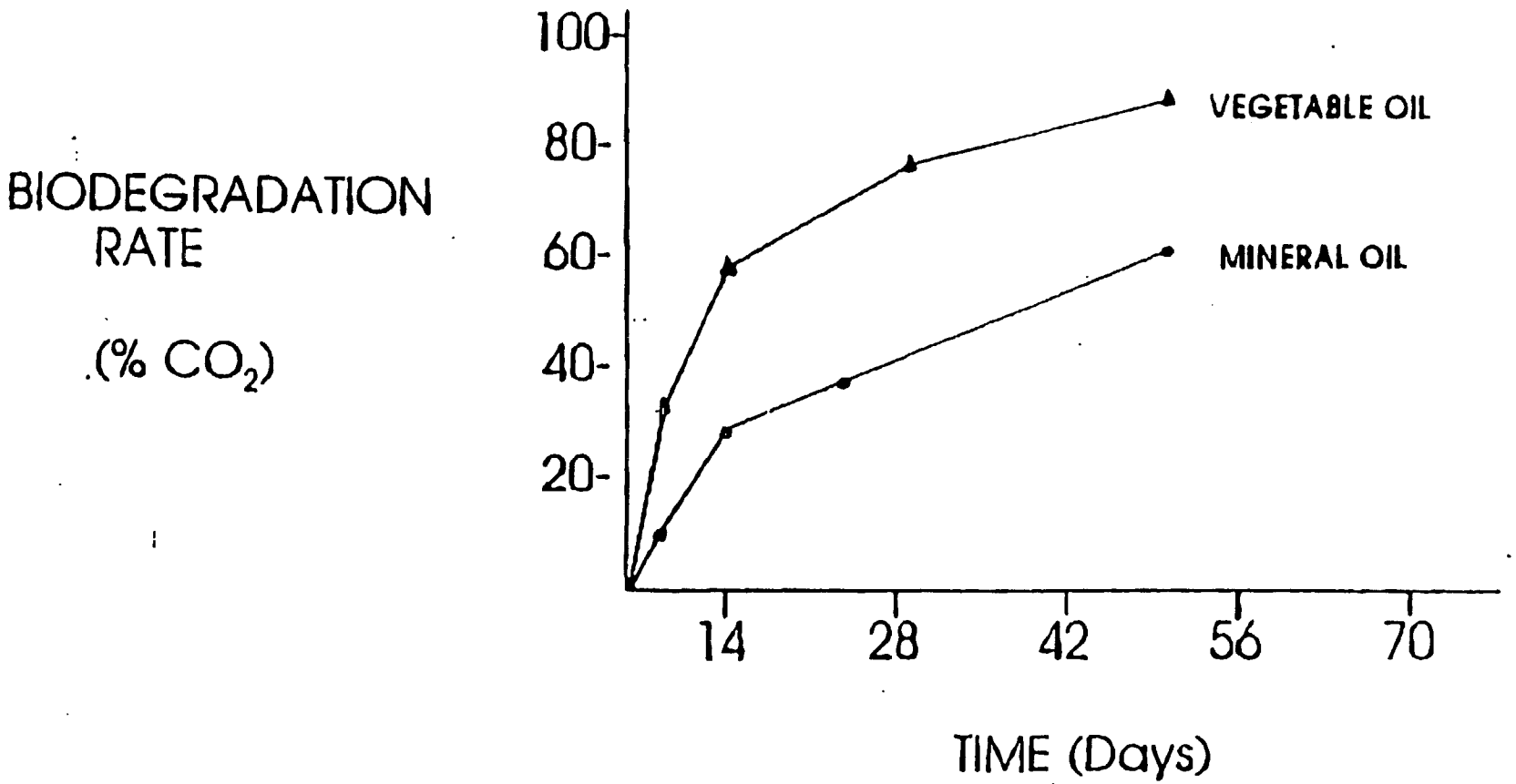
When the facts are made clear, converting hydraulic systems from mineral oil-based technology to vegetable-based materials of questionable environmental benefit, limited recycling capability, and reduced performance makes little sense. As Chevron has recently demonstrated, a mineral oil-based hydraulic fluid can be formulated which is biodegradable, non-toxic, and non-hazardous. However, advanced formulation technology must be combined with responsible use and disposal of such products to ensure preservation of the quality of our environment for future generations.

STANDARD BIODEGRADABILITY TESTS USED

TEST METHOD	DURATION (DAYS)	CRITERIA (%)
READY BIODEGRADABILITY		
OECD 301 A (Mod. AFNOR)	28	>70[a]
OECD 301 B (Mod. Sturm)	28	>60[a]
OECD 301 C (Mod. MITI)	28	>60[a]
OECD 301 D (Closed Bottle)	28	>60[a]
OECD 301 E (Screen)	28	>70[a]
OTHERS		
CEC-L-33-T-82	21	>80[b]
Activated Sludge (OECD 302 A)	28	>20[c]
Zahn-Wellens (OECD 302 B)	28	>20[c]

[a]Classifiable as 'readily biodegradable'.
[b]Meets German 'Blue Angel' requirement for biodegradable hydraulic fluids.
[c]'Inherent biodegradability' tests.

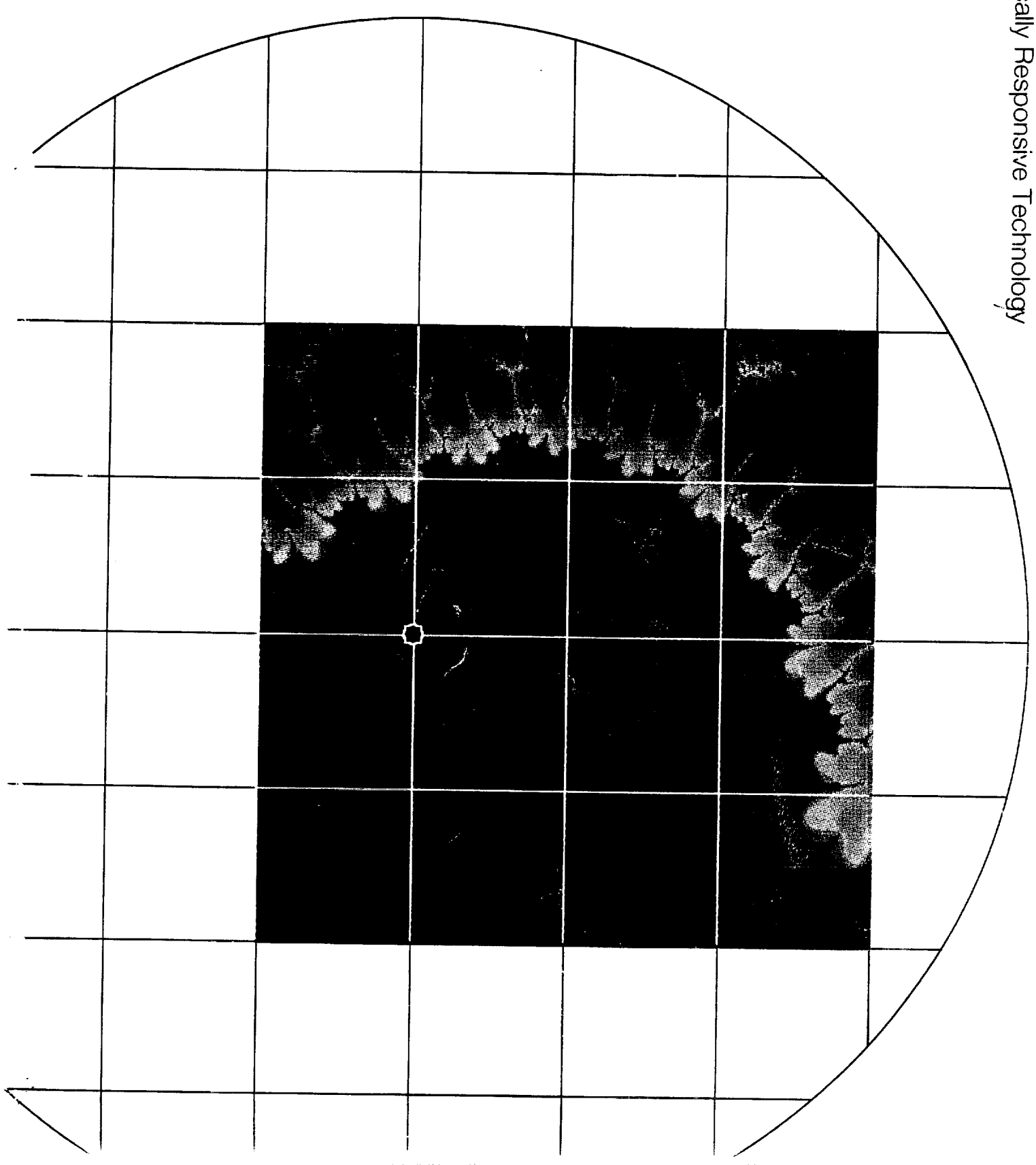
VEGETABLE OIL VS MINERAL OIL BIODEGRADATION RATES



ATTACHMENT D

Biodegradability

Review of the current situation



Lubrizol Ecologically Responsive Technology

BIODEGRADABILITY:

REVIEW OF THE CURRENT SITUATION

Stephanie Harold

April 1993

CONTENTS

Introduction

Biodegradability is not only a property or characteristic of a substance, but is also a system's concept, i.e. a system with its conditions determines whether or not a substance within it is biodegraded.

When material is released into the environment, its fate depends upon a whole range of physicochemical processes and its interaction with living organisms. The most stable compound of carbon is carbon dioxide. All the more reduced organic compounds are themodynamically unstable and will be randomly attacked by microbial enzymes, provided that they have some structural similarity to naturally-occurring substrates.

The California Advertising Statute, amended on the 30th April 1991, states that a manufacturer cannot claim that a product is biodegradable unless it meets the following definition:

"Biodegradable means that a material has the proven capability to decompose in the most common environment where the material is disposed of within 3 years through natural biological processes into nontoxic carbonacious soil, water, carbon dioxide or methane".

Primary Biodegradation

= Minimal transformation that alters the physical characteristics of a compound whilst leaving the molecule largely intact.

Partial biodegradation is not necessarily a desirable property, since the intermediary metabolites formed can be more toxic than the original substrate. Therefore, mineralisation is the preferred aim.

Ultimate Biodegradation

=Complete biodegradation.

Molecular cleavage must be sufficiently extensive to remove biological, toxicological, chemical and physical properties associated with the use of the original product, eventually forming carbon dioxide and water.

The Degradation/Accumulation Expert Group of the OECD Environment Committee have established a series of tests which classify compounds as:

1 **Readily biodegradable**

Rapid and complete mineralisation

2 **Inherently Biodegradable**

20-70% biodegradable in 28 days. Requires "worst possible case" estimates of likely environmental concentrations and therefore further simulation tests may be required.

3 **Non-biodegradable**

Negligible biotic removal of material under test conditions.

FINDING OF NO SIGNIFICANT IMPACT

FOR

Food Additive Petition 5A4440, submitted by Lyondell-Citgo Refining Company Ltd., to amend 21 *CFR* 172.878 to provide for the use of White Mineral Oil, U.S.P., with a minimum viscosity of ISO 100, as a dust control agent for whole, unhulled (rough) rice at an application rate of 800 ppm (0.08% wt).

The Environmental Impact Team, Division of Product Manufacture and Use, Center for Food Safety and Applied Nutrition, has determined that the approval of this petition will not significantly affect the quality of the human environment and therefore will not require preparation of an environmental impact statement. This finding is based on information submitted by the petitioner in an environmental assessment.

Prepared by: William H. Lamont Date: May 27, 1998
William H. Lamont, Chemist
Environmental Impact Team
Division of Product Manufacture and Use

Approved by: Buzz L. Hoffmann Date: May 28, 1998
Buzz L. Hoffmann, Team Leader
Environmental Impact Team
Division of Product Manufacture and Use

94F-0454

FOI/S/

Eurospec (published by EuroLabs Ltd.) make distinctions between ready and inherent biodegradability, defining them to be:

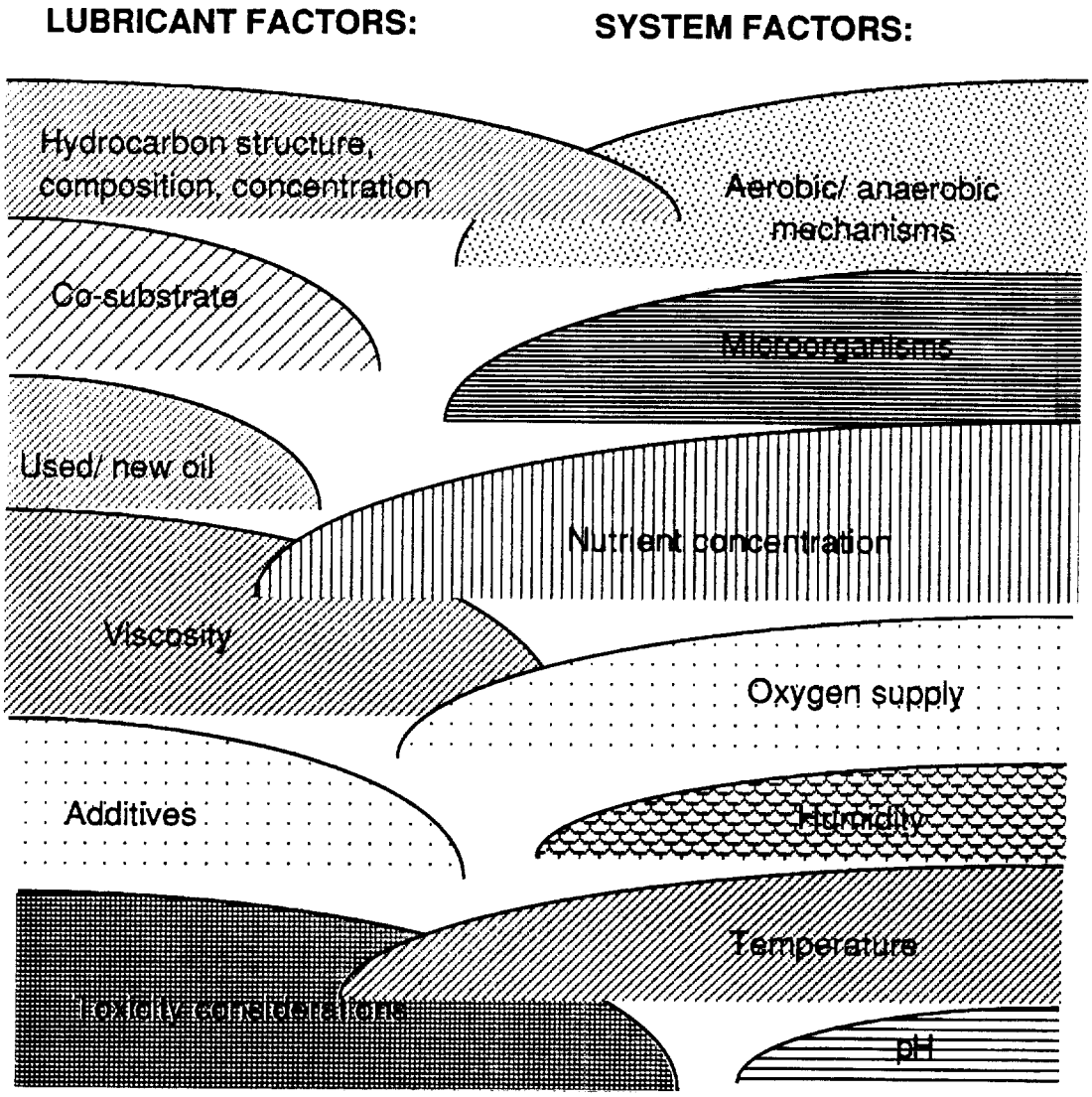
Ready Biodegradability	Inherent Biodegradability
applies to organic substances where, under stringent test conditions, (low numbers of non-adapted bacteria, no other organisms present, relatively high concentration of test substance), greater than 80% of it is removed (primary degradation) or more than 70% of the organic carbon is removed within 28 days (ultimate biodegradation) In the latter case, dissolved organic carbon, BOD and CO_2 are measured in the various internationally accepted test methods. A chemical which passes one of these tests is expected to undergo rapid and ultimate biodegradation in the environment, and no further testing would normally be required.	is used to describe organic compounds which are not readily biodegradable, but over prolonged exposure periods, with adapted organisms and lower concentrations of the chemical, will exhibit levels of degradation similar to those which are readily biodegradable(generally greater than 70% mineralisation of the product) A chemical which shows ultimate biodegradation in this situation is likely to be considered as non-persistent in the environment. If more accurate information is required on the risk to specific environments, it may be necessary to undertake simulation tests. These are longer term projects acting as models for actual situations. They must therefore be validated and justified. A failure to show biodegradation after prolonged exposure, renders the chemical as non-biodegradable or persistent.

Lubrizol Ecologically Responsive Technology

Biodegradability

Summary of factors influencing biodegradation

Biodegradation depends upon the the lubricant and the system conditions:



and will also be influenced by the method of measurement.

When released into the environment, materials either persist or are broken down by a range of mechanisms, including biodegradation. As already discussed, removal of material from the environment can be through either primary (alteration of chemical structure) or ultimate biodegradation (complete oxidation/reduction to simple molecules, i.e. carbon dioxide, water and the production of cells or biomass).

Lubricants may be "readily" or "inherently" biodegradable, depending upon their structure, viscosity, availability of co-substrates, the presence of additives, and whether the oil has been used before:

1 Response of various hydrocarbons to biodegradation ranges from straight-chain alkanes, which degrade very readily, to heavy asphaltic fractions, which tend to be much more resistant.

2 In general, the more viscous the fluid, the slower its degradation, although this may not be the case at lower temperatures.

3 The composition of the oil is important, as certain hydrocarbons which are generally resistant to biodegradation, may degrade in the presence of a co-substrate which encourages the growth of microorganisms in its vicinity.

4 Additives within a lubricant will have an impact upon the degradation of the oil, but it is not always recognised that this can be beneficial in some cases, e.g. dispersants. It is questionable whether zinc dithiophosphates actually enhance overall biodegradation, despite their toxicity.

5 Certain components may exhibit such severe toxicity that they render the immediate environment sterile, and no biodegradation will occur. Thus, it is important to ascertain whether "non-biodegradable" lubricants are truly so, or merely inhibited due to the toxicity of some of their components.

6 Similarly, used oil supports the growth of microorganisms to a greater extent than new oil, since the elevated temperatures to which used oil has been exposed have rapidly accelerated the multiplication of microorganisms.

7 There are two main reaction pathways available for biodegradation, the major one being aerobic, and the other anaerobic. It is a recent and very important finding that aromatic hydrocarbons are subject to anaerobic catabolism. Generally, the rates of anaerobic hydrocarbon metabolism are slow, and to date, consortia rather than pure cultures of anaerobic hydrocarbon degraders have been studied.

These factors relate to the lubricant itself and can be regarded as the lubricant's contribution to its own biodegradation. However, a lubricant cannot degrade in conditions which are adverse to microorganisms, and hence its degradation will be affected by the environment it is discharged into, i.e. freshwater, sea or soil. The soil environment is probably the most complex, being characterised by intimately interwoven solid, liquid and gas phases, a wide range of particle sizes, and a complex chemical composition. Compared with the very uniform marine environment, the physicochemical characteristics of various soil types differ greatly, and classification of soils is still evolving. Freshwater environments are more variable than marine, but less so than soils. Differences between the two extremes of seawater and soil environments are summarised in the following table (PTO).

Parameter	Sea	Soil
Expanse	79% of global surface	21% of global surface
Temperature	-2 to 33C	-40 to 65C
pH	Slightly alkaline 8.4-8.6	Slightly acidic 2.5-11.0
Water Potential	0.98	0 to 0.99
Salinity, %	3.4-3.6	0 to salt saturation; low in most soils
Oxygen availability	Water column usually oxygenated, 8mgO_2/l max.; sediments reduced	Adequately oxygenated except when waterlogged
Inorganic nutrients	N and P limiting	N and P limiting
Organic matter	Extremely dilute; limiting for microbial growth	Relatively abundant, but mainly humus
Attachment surfaces	Few suspended particles	Great abundance of inorganic and organic surfaces
Location of microbial growth	Uppermost surface and sediment	Upper 15cm layer, i.e "plough layer"
Microorganism type	Bacteria, algae, protozoa, fungi; diversity of species low	Bacteria, fungi; high abundance and diversity. Algae and protozoa have limited presence
Typical "total microbial count"	1-100/ml (offshore) 10-1000/ml (inshore)	10^7-10^8/g soil
Counts of hydrocarbon degraders (no pollution history)	< 1-10/ml	10^5-10^6/g soil
Counts of hydrocabon degraders (history of pollution)	Up to 10^4/ml	10^6-10^8/g soil

Typically, mineral oil hydrocarbon biodegrades by 85% after 1 *day* in water, compared to only 24% after 1 *year* in soil. As will be discussed later, this is largely determined by the oil's penetration depth into soil which will vary according to its viscosity and the soil type, but would usually reach 3 to 20cm within 1 to 3 years.

Fundamental to biodegradation is the presence of adapted microorganisms in sufficient quantity. In general, bacteria are the dominant hydrocarbon degraders in marine ecosystems, and fungi and bacteria both predominate in soil. In fact, bacteria are present in most environments, and their metabolic activity is evident in all forms of decay and the building up of nitrogen compounds in the soil through the nitrogen cycle. The microorganisms responsible for biodegradation may be present in the natural environment, and multiply whenever growth substrate is available and suitable conditions prevail, or they may be specifically cultured for that purpose.

Communities exposed to hydrocarbons become adapted, exhibiting selective enrichment and genetic changes which result in increased proportions of hydrocarbon-degrading bacteria. Adaptation implies a selection and proliferation of particular microorganisms, and it can be a lengthy procedure, i.e. several weeks.

Microorganisms cannot survive, and hence biodegradation cannot occur, unless certain conditions are fulfilled:

1 *Liquid* water is a fundamental requirement as it constitutes 80 to 90% of the weight of the microorganism; if frozen, biodegradation is interupted.

2 Carbon substrate, energy substrate and inorganic nutrients for cell growth must be present in the appropriate chemical and physical forms and within certain concentration ranges. Many different organic molecules can act as a carbon source, but some are only suitable for a limited number of organisms, slowing the rate of degradation. The energy substrate for metabolic processes may be derived from the carbon substrate (heterotrophic growth), inorganic molecules or light (autotrophic). For the last two cases, the carbon substrate is then generally carbon dioxide.

3 Nitrogen is also required in substantial amounts by microorganisms and may be assimilated in an inorganic form (nitrogen gas, ammonia, or nitrate) or bound in an organic molecule (e.g. as in an amino acid). Phosphorus and potassium are also essential macro-nutrients for microbial growth. Trace elements such as copper, calcium, boron, and zinc are also necessary but ambient levels present naturally are often sufficient.

4 Temperature, pH, and osmotic pressure must be within the permissable ranges for growth and metabolic activity of microorganisms.

In aquatic environments, rates of hydrocarbon biodegradation are primarily dependent upon the limitation of nutrients, e.g. nitrogen and phosphorus, whereas, biodegradability in soil depends upon oxygen, nutrient and moisture availability, as well as the acidity of the soil. Within the soil environment, light hydrocarbons will be volatilised from the soil surface and the heavier compounds can be degraded slowly by bacteria. Deep within the soil, oxygen is restricted and degradation necessarily becomes anaerobic, which is very slow.

Soil absorption will impair biodegradation according to soil type. Organic chemicals can be subject to biodegradation, chemical degradation, volatilisation, leaching and plant uptake to differing extents, all of which will influence the chemical's long term persistence in soil. Hydrocarbon contamination, although not toxic to plants, can exclude the uptake of oxygen/water and nitrogen by coating the roots of the plants. This is more serious for shallow-rooted plants, such as grasses, and in winter when volatilisation is lower and viscosity is higher. Soils differ markedly in their response to retain heavy metals and organic contaminants in the long term, with many processes occuring simultaneously.

Lubrizol Ecologically Responsive Technology

Biodegradability

Lubricant	Contribution to biodegradation

3.1 Hydrocarbon structure

Petroleum hydrocarbons can be divided into 4 classes:

saturates

aromatics

asphaltenes (phenols, fatty acids, ketones, esters and porphyrins)

resins (pyridines, quinolines, carbazoles, sulphoxides and amides)

Biodegradation occurs by a series of enzyme-catalysed oxidation reactions. A terminal alkyl group is oxidised to an aldehyde, then to a longchain carboxylic acid. After repeated degradation through β-oxidation in the fatty acid cycle to acetic acid and a lower C-number carboxylic acid, the acetic acid is oxidised in the Krebs' (citric acid) cycle to carbon dioxide and water. Hydrocarbons differ in their susceptibility to microbial attack, and in order of their decreasing susceptibility:

n-alkanes >

branched alkanes >

low molecular weight aromatics >

cyclic alkanes

In general terms, biodegradation rates for the saturates >

light aromatics >

high molecular weight aromatics >

polar compounds.

Qualitative relationships have facilitated the synthesis and development of compounds which may be discharged to the environment with reasonable safety, and these may be summarised in terms of hydrocarbon structure.

(i) Straight-chain hydrocarbon degradation

In the aliphatic fraction, n-alkanes can be completely degraded most readily. At high molecular weights, > C18, n-alkanes exist as waxes, and the rate of assimilation is greatly slowed by the problem of mass transfer of solid substances into cells, although n-alkanes up to C44 can be metabolised by mixed populations of soil organisms. The presence of 1 or more double bonds makes olefins more resistant to complete degradation, despite the fact that hydroxylation and epoxidation of double bonds is well known biochemically. Cyclo-alkanes are degraded after adaptation of the microorganisms, and resistance to degradation increases with the number of fused rings in the molecule. Structures with 4 or more condensed rings may be co-oxidised in the presence of a co-substrate.

(ii) Branched hydrocarbon degradation

Branching generally makes an alkane more resistant to biodegradation. Although methyl-branched compounds, e.g. phytane and pristane are degraded by a number of organisms, they tend to be more persistent than other saturates in crude oil.

(iii) Aromatic degradation

Aromatic hydrocarbons are degraded to form aryl acids, but less readily as the number of condensed aromatic rings increase. Some of the intermediates formed are conjugated and exist as water-soluble glucuronides and sulphates.

Ring substitutions can interfere with metabolism; certain of the metabolites produced are known carcinogens. Aromatic functional groups such as hydroxyl and carboxylate groups increase biodegradability, whereas halogen,

nitro and sulphonate groups decrease the rate of biodegradation. *Ortho*-substituted aromatic compounds are slightly more biodegradable than *para*-substituted compounds, and the *meta*-substituted compounds have the least biodegradable substitution pattern.

Only the simplest forms of polycyclic aromatics, (PCAs), i.e. naphthalene, anthracene and phenanthrene can easily support microbial growth. PCAs containing 4 or 5 rings are relatively resistant to biodegradation and previous studies had failed to isolate microorganisms capable of degrading them. A *Mycobacterium* that degrades pyrene and other polycyclic aromatics has now been isolated.

Induction of enzymes for polyaromatic hydrocarbon, (PAH), degradation depends upon lower molecular weight aromatics such as naphthalene. The finding that the enzymes for degrading at least some PAHs are not induced by the substrate itself is important, and may explain the apparent resistance of these compounds to microbial attack. Although cometabolism has been suggested as the mechanism for enhanced rates of 4- or 5-ring PAH degradation in the presence of 3-ring aromatic hydrocarbons in the soil, it is possible that enzyme induction by the simpler aromatic hydrocarbons is important in determining the rates of higher condensed ring aromatic hydrocarbon degradation.

(iv) Asphaltic degradation

The asphaltic fraction is the most resistant to biodegradation and is the most persistent in freshwater ecosystems. Little is known of the metabolism of individual compounds in this fraction. It is probable that some compounds in the asphaltic fraction are not biodegradable, or that they are degraded so

slowly that they should be considered non-degradable. An oil may be removed from an area by physical factors, e.g. tides or currents, or it may be covered over by sediment, but some of its components cannot be metabolised and will persist. Claims that all oil, or more than 50% of heavy crudes, may be removed by microbial metabolism may be exaggerated. Attack on hydrocarbons by oxygenases produces free radicals and other reactive intermediates that may chemically react with each other, forming partially oxygenated, crosslinked, high molecular weight asphaltenes that are quite resistant to further biodegradation. Striking examples of these "synthetic" transformations in the course of petroleum biodegradation are the formation of high molecular weight n-alkanes not originally present in petroleums and the build-up of lipid-rich "petroleum dirt" residue from gaseous methane by methanotrophs. In soils repeatedly treated with oily wastes, a gradual build-up of biodegradation-resistant hydrocarbons can be observed.

Biodegradability is also dependent upon the method of measurement, as outlined in Section 5, but from the CEC L-33-T-82 test, certain trends have been identified:

1 Mineral oils, alkylated benzenes, PIB, PAO's, polyalkyleneglycols have poor biodegradability , i.e. 0-40%

2 Vegetable oils (triglycerides), diesters, polyol esters show good biodegradability, (60-100%). n-Alkyl monocarboxylic acids are common in nature and often appear as products from β-decarboxylation of alkane moieties and they are generally as easily degraded as esters. The degradation products are also more soluble, although the effects on the ecosystem and groundwater contamination are not known.

3 Aromatic polycarboxylate esters range from 5-80%. The same molecule can show consistently wide variation suggesting that competent microflora are restricted in their distribution. Polyethers show poor biodegradabilty in the CEC test, but have the advantage of being water-miscible. Therefore, tests based on oxygen consumption, carbon dioxide evolution or organic carbon removal may be more applicable. By these tests, polyethers are between 0 to 80% biodegradable, depending upon the molecular weight and ethylene oxide/propylene oxide content. Increasing ethylene oxide content and decreasing propylene oxide content give increasing biodegradability.

4 Biodegradability is retarded by the particular alkyl chain lengths (< C4 and > C25) and by the degree of chain branching.

5 Biodegradability depends upon the available nitrogen and phosphorus in the environment and the inoculum size (if the lab test assessment is made after 21 to 28 days). Certain cultures of bacteria utilise tricresyl phosphate and zinc dithiophosphate as carbon and phosphorus sources. N-heterocycles may act as nitrogen sources and, if so, it may be possible deliberately to formulate blends in which the additives might supply the necessary nitrogen, sulphur and phosphorus for total base oil degradation.

6 Additives usually retard the degradation in proportion to their concentration and are themselves poorly degraded, especially heterocyclic structures (triazine, triazole).

Summarising, typical biodegradability values in the CEC L-33-T-82 biodegradability test for common hydrocarbons are:

Mineral oil	15 to 35%
White oil	25 to 45%
Natural and vegetable oil	70 to 100%
PAO	5 to 30%
Polyether	0 to 25%
PIB	0 to 25%
Phthalate and trimellitate esters	5 to 80%
Polyols and Diesters	55 to 100%

3.2 Presence of co-substrates

Cometabolism may be defined as the microbial metabolism of a chemical which does not serve as a nutrient or energy source for that organism. In practice, co-oxidation can occur, whereby non-growth hydrocarbons are oxidised in the presence of hydrocarbons which serve as growth substrates. If this occurs, much greater biodegradation will be observed than would normally be anticipated.

It is not known to what extent cometabolism contributes to the transformation of petroleum components in nature, nor the extent to which populations may be manipulated to enhance this process.

3.3 Used vs. new oil

It has been found that used oil supports the growth of bacteria more readily than new oil, since some oil components are affected during use to become more palatable to microbes.

In a recent study, growth of microorganisms was observed between 30 and 70C (when only the *Bacillus* species could grow); no growth occurred at 80C. Hence heating engine oil to high temperatures decreases the number of microbes, eventually killing or immobilising them at 80C. However, at moderate temperatures, used oil is subject to varying extents of microbial degradation in service, producing metabolites which future microrganisms could use for growth. Different microorganisms are responsible for biodeterioration of oil depending upon whether the oil is hot or cold, since:

Bacteria are the main biodeteriogens of oil when pH = neutral

Moulds and yeast " " " " = acidic

In contrast, new oil has not been previously exposed to microbial degradation and to grow on new oil, organisms must have the requisite enzyme systems to catalyse the initial breakdown of original oil components. Such enzymes are adaptive (inducible) and their production is gradual, i.e. more time is needed for degradation of new oil under optimum conditions.

3.4 Viscosity

Highly viscous oils degrade more slowly than "thinner" oils as shown in a study comparing three grades of oil: 150N

500N

Bright Stock

As anticipated, bright stock was attacked more slowly due to its high viscosity. The rationale for this effect is that hydrocarbon-degrading microorganisms act mainly at the oil-water interface and have been observed growing over the entire surface of an oil droplet. Thus, increasing the surface area of a "thin" oil through its partial dissolution and emulsification should accelerate its biodegradation, but viscous oils are less able to disperse in water.

Note: One implication of this study is that lighter oils may deteriorate faster in storage.

3.5 Additives

There is little incentive to produce biodegradable additives, since the levels at which they are generally used would have a negligible impact upon biodegradability of the total lubricant. Biodegradability is much more a feature of the base oil than the additive package.

However, lubricant additives *can* have a significant effect upon biodegradability, sometimes enhancing it without the additives themselves being biodegradable, (e.g. through the judicious use of dispersants and zinc dithiophosphates), and sometimes impairing it through the toxicity of components towards the microorganisms.

(i) Effect of dispersants

As has previously been stated, considerable microbial activity occurs at interfaces, and there will thus be biodegradative effects associated with the presence of particulates (solid/liquid), emulsions (liquid/liquid), and bubbles (gas/liquid interfaces). Effects associated with particulates and bubble formation fall into the province of "system contributions" to biodegradation, and are thus discussed in Section 4.

Microbial attack occurs mainly through the interface between water, (containing microorganisms), and the hydrocarbon phase. Thus, availability of hydrocarbons is controlled by the area of the hydrocarbon/water interface. Since oil-based lubricants are only sparingly soluble in water, the low interfacial area of oil in contact with water can limit its microbial degradation. All dispersants reduce the interfacial tension between water and oil, thereby promoting the formation of more interfacial area, and increasing the oil's availability to microorganisms. This can be demonstrated simply by adding dispersants to an oil slick. (On the ocean, dispersants work by enhancing the natural emulsifying action of the sea to prevent formation of large agglomerates (tar balls) and a water-in-oil "mousse". Most important dispersants in this application are non-ionic surfactants made up of ethoxylated alkyl phenols, ethoxylated linear alcohols or esters of fatty acids and polyhydric alcohols).

However, not all dispersants enhance biodegradation of oil. Oil-dispersant combinations can cause population shifts in the indigenous microbial community. Many hydrocarbon-using microorganisms produce emulsifying agents, providing evidence of bacterial activity on crude or refined petroleum. Although it is widely held that emulsifiers can be involved in the entry of

hydrocarbons into cells, hydrocarbon degradation can occur without emulsification. Certain dispersant/detergent additives could be detrimental to the movement of organisms and transport of nutrients across the cell membrane, so lowering the rate.

In the laboratory, suspended-growth conditions have proved successful for growing large numbers of microorganisms capable of degrading lubricating oil. Use of dispersant was essential for growing bacteria. Without dispersant, oil would not remain dispersed in the medium, but would form a layer at the top of the reactor or stick to the sides of the glass.

(ii) Effect of Phenates/Sulphonates

Very little information is available on the effect of these chemicals on soils and the ecosystem. One study has shown that with linear alkylbenzenesulphonates (though not necessarily those used in lube oil formulations), about 20% is highly persistent in soil.

(iii) N and P-containing additives

Nitrogen and phosphorus-containing additives may promote the rate of biodegradation if the nutrient medium lacks these elements in adequate concentration to sustain microbial growth.

(iv) Transition and Heavy metals

In general, additive components which contain transition metals have a negative effect. To restrict any food-chain contamination by heavy metals, limits are imposed on the amount of metal-containing sewage sludge applied to agricultural land each year, the maximum values for metals in UK soils are (dependent on pH):

Metal	Maximum permitted levels in water, mg/l	Maximum permitted levels in UK soils, ppm	Typical levels in used oils, ppm
Zinc	50	200	1000
Lead	20	300	2000 (leaded fuel) 200 (unleaded fuel)
Copper		80	50
Chromium		400	30
Nickel		50	
Molybdenum		4	
Cadmium		3	0 to 0.5
Iron			150

For a spill of 5 litres of used oil (as during an oil change), then the heavy metal concentrations would be below the UK permitted levels. However, in certain other European countries, (e.g. the Netherlands, stricter limits are imposed, and the lead concentration (from leaded fuel use only) would be above the "safe" level.

Heavy metal contamination is mainly from atmospheric deposition and consists of lead, cadmium, arsenic, cerium and molybdenum. Group 2 metals, such as zinc and copper can also cause problems as zinc is thought to be toxic to plants (phytotoxic), but is not thought to be a problem at the concentrations involved in a single spill. Repeated spills would increase concentrations and with zinc, accumulation could irreversibly affect the ecosystem. Such contamination is richest in the surface layers.

Lead in plants is mainly from deposition onto foilage, and vehicle emissions account for about 90% of atmospheric lead. High levels of lead can induce negative effects on the microbial processes in soil; this has an implication for the longterm fertility of soil through the microbially mediated processes of nutrient cycling (primarily nitrogen and phosphorus).

Heavy metals have exceedingly long residence times in soil because migration out of the surface (ploughed) layer is extremely slow and removal as crop uptake, very inefficient. No definite relationship has been found in soil between soil lead and cadmium levels in low concentrations, representative of rural soils and plant uptake. Discharge of oil into water produces more dramatic results, since if the oil can form a *static* film on top of the water, exchange of oxygen between air and water may be prevented. Heavy metals can poison water treatment processes and aeration of hydrocarbons can potentially use up the available oxygen, suffocating fish.

(v) PCAs

The polynuclear aromatic (PCA) content of used motor oils can be as high as 1 to 3%. This implies that a small localised spill of 5 litres is equivalent to between a 100 to 300 fold increase in PCA concentration over that from the application of sewage sludge. The effect of this higher concentration on soil quality and the ecosystem has yet to be studied.

PCAs commonly contaminate soils and are listed as known or suspected carcinogens on the US Environmental Protection Agency (EPA) and EC priority pollutants' lists. Field measurements have shown that it takes about 8 years for half of the PCA material to be removed from soil via volatilisation, chemical breakdown, leaching, biodegradation and plant uptake. The most

persistent components are benzoperylene, coronene, and benz–β-fluoranthene (which is highly carcinogenic).

Volatilisation is only significant for naphthalene, and for larger compounds (more than 3 rings), biodegradation is the key process. Retention to soil organic matter (humus) will affect any volatilisation, and persistence in soils generally increases with molecular weight.

PCA compounds are unlikely to contaminate the water table, as those which could potentially reach the ground water are also easily lost or degraded. Similarly, plant uptake of soil PCA is unlikely, so that PCA will not be incorporated into the food chain, but may still affect plant growth.

(vi) PCBs

Polychlorinated biphenyls (PCBs) have acquired a certain notoreity due to their widespread presence and persistence. They are present in UK soils at concentrations up to 100ppm (typically 2 to 50ppm). Destruction of PCBs is normally achieved by high temperature incineration, as microbial breakdown is difficult and has only been achieved in the laboratory.

3.6 Toxicity Considerations

(i) Toxicity of Used Engine Oil

AMES testing has determined *in-vitro* predictive tests for mutagenicity of used engine oil. 70% of the effects are caused by polyaromatic hydrocarbons (PAH) with >3 rings, although this fraction represents only 1% of used oil. Of this highly mutagenic fraction, 18% of the effect is caused by benz–α-pyrene.

(ii) Measurement of Toxicity

One of the problem areas which needs to be addressed is that of distinguishing between true non-biodegradability and inhibited biodegradability as a result of toxicity of the substances tested. Where biodegradability is being assessed, the test concentrations used are generally much higher than any predicted environmental concentration. If these concentrations are toxic to the test system, then a negative result in a biodegradability test is liable to be misleading.

To avoid toxicity to the sludge, biodegradability testing should be made at 10% of the EC50 value, bearing in mind that:

(a) Compounds with an EC50 value greater than 300mg/l are unlikely to be toxic in ready biodegradability tests;

(b) Compounds with an EC50 value of less than 20mg/l may pose problems necessitating the use of the stringent Closed Bottle test, or the use of ^{14}C labelled compounds;

(c) Compounds with an intermediate EC50 of between 20-300 mg/l need to be evaluated at a range of concentrations in biodegradability tests, or may need to be evaluated carefully to define the precise no-effect level.

A variety of microbial tests are used to assess the toxicity of chemicals, employing suppression of growth, substrate utilisation, enzyme activity and oxygen uptake as a measure of toxicity, but at present, no firm guidance has been given as to which test or tests are most appropriate for biodegradability testing.

Procedures must distinguish between the inhibition of biodegradability and inertness of the test substance. Various studies have been conducted and sample chemicals were evaluated in a variety of tests to assess their toxicity to aerobic sludge organisms. The tests employed were:

BOD_5

Closed Bottle Inhibition Tests

Inhibition of Respiration of Activated Sludge

Growth Inhibition of Activated Sludge

Light Emission from *Photobacterium phosphorem* (MICROTOX test)

Repetitive Die-away test

Results from these tests were compared with results obtained from a number of ready biodegradability tests using the sample compounds at anticipated non-toxic and toxic concentrations. None of the test methods evaluated consistently forecast the toxicity of the chemicals, e.g. the MICROTOX and nitrification inhibition tests were too sensistive. It was concluded from this study that a combination sludge respiration rate and/or growth tests seemed most appropriate.

ECETOC initiated a limited study aimed at comparing a number of the most common methods used to define the toxicity of chemicals. A range of chemicals was selected which were known to be either toxic or apparently resistant to bidegradation, and to have given variable results in biodegradation studies. It is questionable whether the test conditions in the variety of methods available to determine the toxicity truly reflect the conditions in any of the ready biodegradable test procedures.

For example, the OECD sludge respiration inhibition test (OECD, 1984) is performed at high bacterial concentrations and over a short period; it measures the effect on perspiration and not on growth. The turbidity test (1985) is performed at low bacterial concentrations and probably measures growth of the least sensitive species. BOD inhibition (BOD/I) and Closed Bottle Inhibition tests measure the effect of a test substance on the degradation of glucose or other appropriate substrates, but this may not reflect the effects of the test substance on those species responsible for degrading it. Test methods using single species, or specific activity (e.g. nitration) may also have an inappropriate sensitivity for toxicity screening purposes. Although in the AFNOR (OECD, 1981) and RDA (1979) tests, a toxicity control experiment is included, this uses an additional substrate and a

shorter period of incubation and the degree of inhibition may not represent the degree of suppression of the biodegradation potential of the inoculum.

(iii) Legislation

Despite areas of controversy, ecotoxicological legislation is being adopted in many countries, and the major legislative initiatives in recent years include:

1973 Japan passed ecotoxicological legislation

Toxic Substances Control Act (TSCA) passed in USA.

1979 EEC passed 6th Amendment

Australia, Canada, Finland, New Zealand, Norway, Switzerland and most other OECD (Organisation for Economic Co-operation and Development) countries are likely to follow suit.

WGK (Water Hazard Classification) is a German model for assessing the effect of functional fluids on the aquatic environment via mammalian acute toxicity, fish toxicity, and biodegradability. It grades fluids from 0 to 3.

1989 List concerning classifications into water-endangering classes was published.

System

Contribution to biodegradability

Lubrizol Ecologically Responsive Technology

Lubrizol Ecologically Responsive Technology

System	Contribution to biodegradability

Biodegradability

Lubrizol Ecologically Responsive Technology

System	Contribution to biodegradability

4.1 Microorganisms

Hydrocarbon degradation by microbial communities depends upon the composition of the community and its adaptive response to the presence of hydrocarbons. Bacteria and fungi are the key agents of degradation, with bacteria assuming the dominant role in marine ecosystems and fungi becoming more important in freshwater and terrestrial environments. Hydrocarbons are degraded by many species of bacteria and fungi; 22 types of bacteria have been identified and 31 types of fungi.

Bacteria utilise a wider range of hydrocarbons,including cycloparaffins and aromatics, and they respond more quickly to high oil concentrations. Fungi tend to persist longer and be more tolerant of adverse environmental conditions. Bacteria and yeasts are less able to degrade long chain alkanes, whereas filamentous fungi do not preferentially degrade any particular chain length. Key to rapid biological decontamination is having a large population of active hydrocarbon degraders because the oil concentrations can be high and an immediate response is needed.

The rate at which microorganisms grow and consequently degrade materials is characterised by two distinct phases. During the "lag phase", growth is slow. The organisms manufacture certain enzymes and also prepare an environment for future growth by excreting metabolites into the growth medium. The "log phase" sees exponential growth, where the entire population may double in a matter of hours.

Compared with what is known about bacteria, very little is known of the interactions between petroleum hydrocarbons and algae, yeasts and filamentous fungi. Fungi are common in rivers, mesotrophic and eutrophic lakes and some aquatic fungi can oxidise PAH. Appropriate enrichment cultures yield filamentous fungi that can degrade crude oils and grow on petroleum hydrocarbons. It has been reported that although bacteria initiated the degradation of a mixture of hydrocarbons, almost twice as much was degraded when yeasts and other fungi were also present.

Microorganisms that degrade aromatic hyrocarbons may be distinct from those that attack aliphatic hydrocarbons. Microbial isolates that utilize hexadecane cannot grow on phenanthrene, and *vice versa.* Thus, the degradation of different classes of hydrocarbons may be carried out by totally different populations of microorganisms.

Petroleums added to an aquatic ecosystem generally cause an enrichment for hydrocarbon-using microorganisms. Hence, it would be expected that biodegradation of petroleum would occur more rapidly in systems receiving chronic petroleum pollution than in pristine systems which receive a single oil spill. Enrichment on one type of petroleum does not necessarily select for organisms that can degrade another petroleum. Adapted communities, i.e. those which have been previously exposed to hydrocarbons, exhibit higher biodegradation effects than those with no history of hydrocarbon contamination. The mechanisms of adaptation include both selective enrichment and genetic changes, resulting in a net increase in the number of hydrocarbon-utilizing organisms and in the pool of hydrocarbon-catabolizing genes within the community. The association of such genes with plasmid DNA may also lead to an increased frequency of plasmid-bearing

microorganisms. Seeding of petroleum-contaminated water or soils with hydrocarbon-utilizing bacteria has met with some success, particularly in situations in which chemostats or fermentors have been used to control conditions and reduce competition from indigenous microflora.

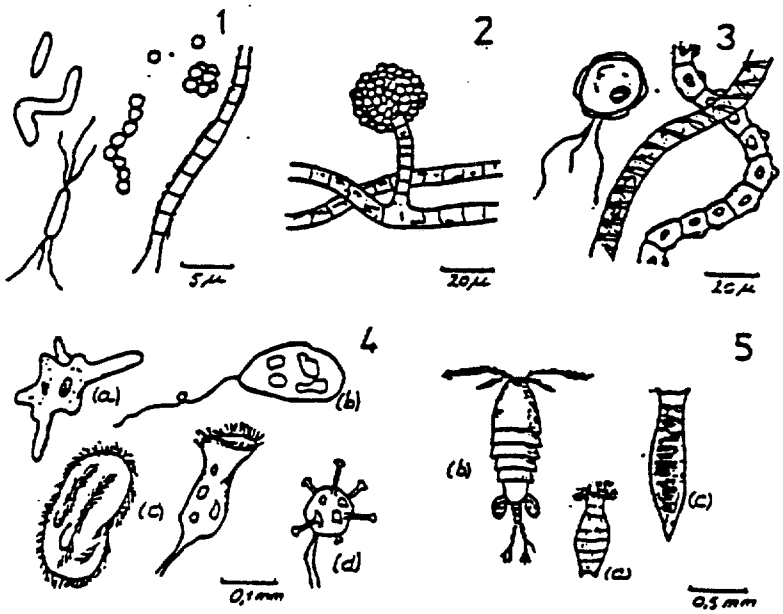


Figure 1. Microorganisms. *1*, bacteria; *2*, fungi; *3*, algae; *4*, protozoa; and *5*, higher microorganisms.

4.2 Nutrient Concentration

Oxygen consumption depends upon the phosphate concentration in freshwater lakes. Oil provides an energy source for microbial growth in the form of carbon to initiate a rapid increase in the number of microorganisms. Nitrogen is needed to sustain this growth as it is a component of protein and nucleic acids.

A modified CEC L-33-T-82 test was conducted in which river water was concentrated to 10^3 c.f.u/ml (see Section 5). Initial degradation in the "no N_2" flask was probably due to nitrogen being present in lake water inoculum, as increasing nitrogen was seen to give increased biodegradation, the trend continuing until an optimum C:N ratio was reached. After this, increasing nitrogen made no difference. Therefore, results from labs using inoculum with high nitrogen levels (from agricultural fertilisers etc.) would be higher than those generated in labs using inoculum from non-agricultural areas.

Microbial attachment to organic and inorganic particles is common in freshwater and marine ecosystems. In freshwaters, the density of attachment varies, but there are probably more attached bacteria in freshwater systems than in marine systems. Particulates may concentrate nutrients and act as nutrient buffers, thereby stimulating bacterial growth even when they contain no detectable nutrients. Both detrius and particles of clay can enhance microbial activity. By secreting organic matter, bacteria can increase the size of particles whilst attached. Bacteria and fungi can be involved in aggregation and decomposition of detrital particles.

4.3 Oxygen supply

Hydrocarbons are highly reduced substrates and their metabolism requires an electron acceptor. Oxygen, nitrogen and sulphate are the most common, but pathways that use oxygen are by far the most important in nature and biochemical pathways for the metabolism of petroleum hydrocarbons generally involve insertion of oxygen at an early stage.

The initial steps in the catabolism of aliphatic, cyclic and aromatic hydrocarbons by bacteria and fungi involve the oxidation of the substrate by oxygenases, i.e. there is a need for oxygen. Aerobic conditions are therefore necessary for microbial oxidation of most hydrocarbons in water. (3 to 4g of oxygen is required for complete oxidation of 1g of alkane and degradation of 3mg of oil would require all the oxygen present in 1 litre of water).

Oxygen is present in the upper levels of the water column in marine and freshwater environments. Aquatic sediments are anoxic except for a thin layer at the surface of the sediment. Most interfaces have a net negative charge and attract cations and macromolecules. The bacterioneuston microlayer is c. 1μm thick and some bacteria have a greater tendency than others to accumulate there. Bubble formation enables transport of ions and macromolecules to the surface. Adsorptive bubble separation is referred to as the "adsubble process", which can result in selective concentration at the water surface of bacteria derived from the water column.

2 pints of motor oil create a slick of 1 acre in water, but an oil slick is not a bar to the transfer of oxygen to underlying water. Most lakes and rivers are aerobic, but oxygen can be limiting in eutrophic lakes and in the hypolimnion and metalimnion of stratified lakes. Most bottom sediments are anaerobic 1 to

2 cm below the surface and petroleum components that reach the bottom and are covered by silting or sedimentation are metabolised very slowly.

Bioturbation, or mixing, of sediments by worms and other benthic organisms increases aeration and provides a mechanism for speeding up the metabolism of natural hydrocarbons in sediments. Thus, toxic hydrocarbons from petroleum that kill benthic macro-organisms inhibit bioturbation and retard hydrocarbon degradation.

4.5 Temperature

Temperature often is not the major limiting factor for hydrocarbon degradation, except that it relates to other factors such as the physical state of the oil and whether water is available in a liquid form for the microorganisms. Temperature affects the physical state of hydrocarbons, some of which undergo solid/liquid phase transitions within the range of temperature changes in natural ecosystems. It also affects the solubility of petroleum hydrocarbons, most of which are sparingly soluble at best. Small alkanes are more soluble in water at 0C than at 25C, and some are less soluble.

Temperature has a further impact upon the fate of petroleum hydrocarbons in aquatic ecosystems as it profoundly affects the growth of microorganisms. Moreover, the hydrocarbon-using microbial population in an aquatic ecosystem is not necessarily adapted optimally to the temperature of the ecosystem. As temperature increases, enzymatic reactions and metabolic rate increase until a temperature is reached when proteins become denatured. Optimum growth occurs at 20-25C and the CEC test conditions are adjusted accordingly. Using a modified CEC test, with river water

concentrated to 10^5c.f.u./ml, the biodegradable lubricant degrades 3 times faster at 25C than at 5C.

Many lakes never reach 25C and thus field degradation is likely to be lower. Changes will be seen in degradation rates throughout the year, with little occuring in winter and more in the summer. The effect may be compensated for by seasonal changes in the population of microbial communities capable of low temperature utilisation. Petroleum biodegradation has been observed to occur at temperatures as low as -1C, but the fastest rates occur above 20C. Freezing of the solution water interupts biodegradation, while higher temperatures can increase membrane toxicity.

As well as slowing the growth rate of microorganisms, low temperatures may retard the rate of volatilisation of low molecular weight hydrocarbons, some of which are toxic to microorganisms. This would delay the onset of biodegradation at low temperatures and a significant lag phase has been noted before the onset of hydrocarbon degradation for the lighter oils. No toxic volatile fraction was associated with the heavy oils. At low temperatures, it appears that co-metabolism plays an important role in determining the rates of disappearance of hydrocarbons.

4.7 Aerobic/ Anaerobic mechanisms

Anaerobic degradation of hydrocarbons is of little ecological importance in freshwater ecosystems. Most organisms cannot grow on 1-alkenes, the proposed intermediate for the anaerobic metabolism of alkanes. Organisms require an enzymatic mechanism which permits addition of water across the double bond, forming a secondary alcohol.

However, methane activation may occur in lakes either aerobically (when oxidised methane is assimilated into cellular material), or anaerobically. For the anaerobic pathway, sulphate may be used as an electron acceptor to oxidise, but not assimilate, methane to carbon dioxide. Acetate may serve as a source of assimilable carbon, but is not oxidised to carbon dioxide through this route. Nitrate would not act as the electron acceptor for anaerobic degradation.

4.9 Chemical and Photochemical Degradation

Components of petroleum may undergo abiotic chemical or photochemical oxidations in the environment. Generally, autoxidation of organic compounds occurs through free radical formation by thermal or photochemical excitation, possibly aided by the presence of light-absorbing photo-sensitisers. Metal ions and some organosulphur compounds may act as catalysts in generating free radicals from hydrocarbon molecules. Thermal degradation of hydrocarbons is negligible at environmental temperatures below 80C, but studies have shown photochemical oxidation to play a significant role in degrading petroleum in aqueous environments.

Much of the preceding information on the effects of a freshwater environment upon biodegradability applies to seawater, with some additional comments:

4.1 Microorganisms

The most important hydrocarbon-degrading bacteria in both marine and soil environments are *Achrombacter, Acinetobacter, Alcaligenes, Arthrobacter, Bacillus, Flavobacterium, Nocardia and Pseudomonas* spp and the coryneforms. *Vibrio* spp. is limited to the marine environment.

Among the fungi, *Aureobasidium, Candida, Rhodotorula*, and *Sporobolomyces* spp. are the most common marine isolates and *Trichoderma* and *Mortierella* spp. are the most common soil isolates. Hydrocarbon degrading *Aspergillus* and *Penicillium* spp. have been frequently isolated from both environments.

4.2 Nutrient Concentration

Nitrogen is limiting in sea water and the rate of oxygen consumption depends upon the available nitrogen, i.e. the phosphorus/nitrogen ratio. In general, sea water provides sufficient nitrogen to degrade 30g of oil per year at summer temperatures and 11g of oil per year at winter temperatures. Without added nutrients, aromatic hydrocarbons are more readily attacked than saturated hydrocarbons by marine and soil microbes. Addition of nitrogen and phosphorus stimulates degradation of saturated hydrocarbons more than that of aromatic hydrocarbons.

4.5 Temperature

In seawater, hydrocarbon degradation occurs at temperatures as low as 0 to 2C. Due to the great mass and high heat capacity of seawater, the range of temperature extremes is rather limited. On a worldwide basis, ocean water temperatures attain a range of 35C, compared with more than a 100C spread for soils. At a single location, sea water temperatures rarely vary above 25C over the year.

4.10 Salinity and Pressure

There appears to be a general reduction of metabolic rate at extreme salinities (> 20%) and it is doubtful whether biodegradation can progress in hypersaline conditions. Microbial degradation of hydrocarbons in the deep sea has been found to be restricted due to high pressure levels, and it appears that oil entering deep ocean environments will be degraded very slowly and persist for long periods of time. Typically, the *in situ* oil biodegradation rates of marine environments exposed to oil on a chronic basis, range from $5x10^{-4}$ to 0.6g/kg of seawater/day, corresponding quite closely to soil data (see later).

System

Contribution to biodegradability

brizol Ecologically Responsive Technology

Soil

4.1 Microorganisms

Soils vary greatly in their suitability as microbial habitats, but discounting such extreme cases as desert, perma-frost, saline or highly acidic soils, then of all natural environments, soils are the richest microbial habitats. Plentiful organic substrates and attachment surfaces in the soil environment encourage the proliferation and diversity of microorganisms. In fertile soils, viable microbial counts range between 10^7 and 10^8/g of dry soil, while direct counts are as high as 10^9/g. Bacteria and fungi are the principal agents of petroleum biodegradation in soil, but the relative contribution of these groups to the process is not yet clear. Algae and protozoa are constrained by the lack of light penetration and scarcity of free water and are present in relatively low numbers. In fertile soils, bacterial biomass may comprise 0.015 to 0.5% of soil mass, whereas fungal biomass may reach 0.05 to 0.5%.

Petroleum addition to soil selectively enriches that sector of the microbial community able to adapt and utilise new substrate. Changes in the geophysical environment creating additional selective pressures may ensue. Petroleum percolation through the soil reduces aeration and upsets the carbon/inorganic nutrient balance for indigenous populations. Any toxic components of petroleum may selectively inhibit members of the microbial community, producing shifts in population size and species' diversity within soil. In deeper soil strata, where anoxic conditions develop, anaerobic activity may play a significant role in degrading hydrocarbon metabolites produced in the overlying soil layer by aerobic microorganisms.

It is difficult to generalise about the microbial response of soils subjected to oil contamination. The literature seems conflicting due to the great diversity of soils and petroleums studied in different climates. Certain common trends are apparent however:

1 Microbial numbers and activity are enhanced in contaminated soils. Stimulation of microbial activity is positively correlated to increasing amounts of hydrocarbons in soil, up to a level of 5%. Although higher concentrations of hydrocarbon generally do not enhance biodegradation rates, it has been reported that soils receiving the largest application (39%) of crude oil possessed the highest number of microorganisms.

2 The potential toxicity or inhibitory effect of petroleum hydrocarbons does not necessarily manifest itself in soils where biodegradation conditions are favourable.

3 Most toxic components may volatilise or become immobilised by sorption to soil organic matter, although partial degradation of hydrocarbons may emulsify and release more harmful substances into the environment. The great absorption capacity of soil for both polar and non-polar materials reduces the effective toxicity of all chemicals in soil. This means that the same concentration of a toxic hydrocarbon, such as cyclohexane or toluene, is less likely to inhibit microbial activity in soil than it would in an aquatic environment.

4.2 Nutrient Concentration

Depending upon the fertility of the soil, addition of nutrients can be necessary to allow maximum degradation rates. When the soil is infertile and hydrocarbons are easily degraded and in high concentration, nutrient addition stimulates degradation; little or no stimulation from nutrient addition will be seen otherwise.

With respect to heterotrophic microbial activity, the soil environment, much like the ocean, is usually limited by organic carbon. Although top soils have vastly more organic carbon per unit volume than ocean water, this organic carbon is humified and not readily available for mineralisation. However, early composting studies revealed that if soil is amended by large amounts of nitrogen-free carbon substrate, e.g cellulose, nitrogen and eventually also phosphorus become limiting in the build-up of microbial biomass and thus the composting activity.

The situation is very similar in the case of an oil spill which provides carbon, but no other nutrients. In most cases, oils are deficient in nitrogen, phosphorus and other macro- and micro-nutrients. It has generally been found that immediately after addition of nitrogen and phosphorus salts, oil biodegradation is strongly stimulated in contaminated soils. The situation in soil is more complex than at sea where nitrogen and phosphorus supplements consistently have a positive effect on oil biodegradation.

Nitrogen-defiency of some oil-contaminated soils provides dinitrogen-fixing microorganisms with a selective advantage. Selective enrichment for nitrogen-fixing bacteria may provide significant amounts of nitrogen to naturally nitrogen-poor soils. However, this process is slow and leads to

humus-bound rather than readily available nitrogen. In the short-term, it is not able to provide sufficient nitrogen to relieve this nutrient limitation in oil-contaminated soil. Addition of nitrogen and phosphorus usually increases oil biodegradation, but its impact is most obvious on the hydrocarbons which are structurally most biodegradable.

Oil or emulsified oil may adsorb to detrius or to larger particles which affects the final factor controlling the rapid degradation of hydrocarbons i.e. their availability to microorganisms. Due to their hydrophobic nature, hydrocarbons are found sorbed to soil particles, or in a separate phase, but their dissolved concentration is low.

4.3 Oxygen supply

The availability of oxygen in soils is dependent upon rates of microbial oxygen consumption, soil type, waterlogging and the presence of utilisable substrates which can lead to oxygen depletion. The initial steps of hydrocarbon biodegradation are oxygen-dependent; sulphate, a potential electron acceptor, is not abundant in soils and nitrate is not energetically favourable for this purpose.

The highest rate of oil degradation occurs when aeration is maximised. Tilling the soil provides immediate aeration and opens the soil structure. Aeration status of the soil depends upon the total amount of air-filled pore space, size of pores, rate of oxygen consumption and the geometric distribution of the oxygen consuming soil layer. Large amounts of air-filled pore space and the large size of the pores ensure high oxygen reserves and rapid replacement of oxygen by diffusion. Elimination of air-filled pore space, e.g. by water-logging, decreases the soil oxygen reserves to a small amount dissolved in soil

solution. In fine-textured heavy clay soils, the small size of the pores slows oxygen diffusion, and partial or complete water saturation aggravates the situation.

Large amounts of rapidly utilisable organic substrates, including hydrocarbons, tend to deplete oxygen reserves of soil, especially if the small pore spaces or a high density of water saturation slows oxygen replacement by diffusion. The thicker the oxygen-consuming soil layer is, the slower is the rate of oxygen diffusion to the deeper layers. The upper few cms of hydrocarbon-contaminated soil may remain aerobic, while its deeper layers become anoxic. A high soil water table contributes to the development of anoxic conditions in the subsoil.

4.4 Humidity

Moisture is essential to active life processes, but too much moisture interferes with the availability of oxygen. Aerobic conditions are essential for rapid degradation of hydrocarbons, since oil-oxidisers require oxygen. Saturation of soil pores with oil or water decreases ventilation and can slow degradation. Thus, there must be a favourable balance of water:oxygen levels to ensure survival of the microorganisms.

The moisture status of soil is best expressed in terms of a percentage of its moisture -holding capacity. At 100% saturation, all available capillary pore spaces are filled with water. At 10% of the water-holding capacity, osmotic and matric forces prevent sufficient water reaching the microorganisms, so that metabolic activity becomes marginal. 50 to 80% saturation is optimal for aerobic microbial activity.

4.5 Temperature

In frozen soil, no oil biodegradation occurs and thus the overall persistence of oil in Arctic soils is very long. Hydrocarbon-degrading microorganisms isolated from frozen soils are able to grow at 5C. Fungal isolates generally require 10C for growth. At a single location, soil temperatures can vary by 50C for a temperate-zone soil.

4.6 pH

Whilst the pH of marine environments is uniform, steady and slightly alkaline, pH values of various soils encompass a wide range, but most of them are somewhat acidic. The marine environment is well buffered against acidification by its carbonate-bicarbonate system, as are some, but not all soils. In the latter case, organic or mineral acids from various metabolic processes, can lower soil pH to rather extreme values.

Most bacteria have limited tolerance for acidic conditions; fungi are more resistant. Therefore, the soil pH will influence what type of microorganisms can participate in hydrocarbon degradation. In addition, there is evidence that the overall rate of hydrocarbon degradation is higher under slightly alkaline conditions than under acidic conditions. In acidic soils, most hydrocarbon degradation is carried out by fungi. Carbon dioxide evolution is stimulated in polluted soil, suggesting that at low pH, fungi are important in hydrocarbon biodegradation. However, the overall rate under low pH conditions is lower than the rate attainable by a mixed bacterial-fungal community at neutral or slightly alkaline pH.

4.7 Aerobic/ Anaerobic Degradation

Anaerobic metabolism of aromatic hydrocarbons has recently been demonstrated after years of controversy. Previous work indicated that anaerobic degradation of petroleum hydrocarbons by microorganisms was negligible. Limited anaerobic degradation had been observed of oxidised aromatic compounds such as the benzoate end of halogenated aromatic compounds e.g halobenzoates, chlorophenols and polychlorinated biphenyls.

Recent evidence indicates that microbial consortia from soil and sludge can metabolise unsubstituted and alkyl-substituted aromatics, including benzene, toluene, xylene, 1,3-dimethylbenzene, acenaphthene and naphthalene in the absence of oxygen. Hydroxylation of the aromatic ring of toluene and benzene is believed to depend upon water as the source of oxygen. DNA probes have been used in the analysis of genetic adaptation of microbial communities upon exposure to aromatic hydrocarbons. Expansion of the DNA probe method should revolutionise the study of the microbial degradation of hydrocarbons in the environment. It may be possible to select, via genetic engineering, bacterial and fungal strains, capable of eliminating hydrocarbon pollutants.

The importance of anaerobic biodegradation of aromatic hydrocarbons in the environment is unknown and further studies are required to elucidate anaerobic pathways, as well as to determine whether other hydrocarbons, such as alkanes, and hydrocarbon mixtures, such as crude oil, can be fully degraded under denitrifying or methanogenic conditions.

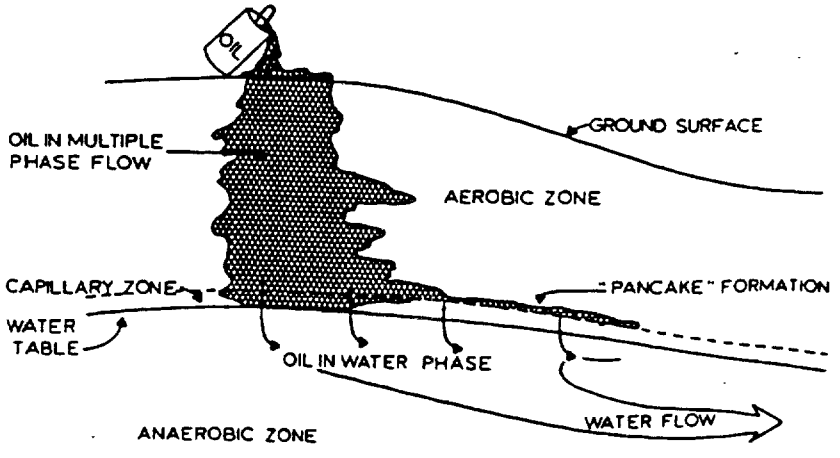
4.8 Distribution, Volatilisation and Leaching

Physical distribution of petroleum spilled onto soil affects its impact on, as well as its removal from, the contaminated environment. Lateral spreading along the surface increases the contaminated area, but also facilitates evaporative removal of low molecular weight hydrocarbons. Vertical penetration is mediated by gravitational and capillary forces, but its effect is to decrease evaporation, reduce the availability of oxygen and possibly contaminate groundwater. Oil contaminants that percolate deep into the soil and to the water table are very difficult to clean up. Deep infiltration is most likely to occur in the case of low viscosity oils, gasoline, kersosene, light heating oil and light crude oils on highly porous sandy or gravelly soils.

(i) Distribution

The area of contaminated soil depends upon several factors including volume of the spill, oil viscosity, temperature, land contour, soil porosity, surface roughness, and even factors such as litter, plant cover and weather conditions.

Figure 2 Schematic representation of soil infiltration, distribution and subsurface movement of an oil spill. After Somers, 1974, and Vanlooke et al., 1975.



If soil is impermeable to oil (due to freezing, water saturation, or extreme compaction) and if the surface is flat:

$$r = (Q/\pi h)^{1/2} . t^{1/2}$$

r = radius of oil spill at time t

Q = rate of spillage

h = thickness of oil layer

t = time

If the surface is permeable, the horizontal spread of the oil is reduced by the amount that the oil infiltrates into the soil (vertical movement):

$$r = Q[r_c \gamma \cos\theta / 2\mu\pi]^{1/2} \cdot t^{1/4}$$

r_c = radius of soil capillaries

γ = surface tension at the oil/water interface

θ = angle of contact between oil and solid, expressing wettability of the soil particles by oil

μ = oil viscosity

In porous soils:

$$\text{Spill area } (m^2) = 53.5[\text{spill volume } (m^3)]^{0.89}$$

(ii) Volatilisation

Compared with the marine environment where evaporation from the water surface is a major mechanism for initial petroleum removal, infiltration into porous soils limits and slows evaporative loss of volatile hydrocarbons. 20 to 40% of crude oils may volatilise from the soil. Higher summer temperatures, extensive lateral spreading over impermeable surfaces and adsorption onto surface vegetation may enhance petroleum volatilisation to such levels. Evaporation is greatest when contamination of moist soils occurs

at high temperatures, since the upward movement of soil water limits oil infiltration and promotes evaporation.

Other field studies demonstrated that < 0.1% of crude oil and only 0.6% of machine coolant oil evaporated from the soil. This is probably the rule in temperate arable soils where oil is rapidly absorbed into the surface strata and migrates downward into the subsurface layers. At ambient temperatures, n-alkanes > C18 exhibit no significant volatilisation, and lighter, less viscous oils containing a high percentage of volatile hydrocarbons penetrate quickly into soil where volatilisation is negligible. The rate of evaporation is determined by temperature, oil composition, wind speed, solar radiation and thickness of the oil layer, but the latter three have little effect on oil evaporation within the soil matrix.

(iii) Leaching

Movement of oil in freshly contaminated soil generally occurs as a multiple phase flow, where oil and water are immiscible. As hydrocarbons become emulsified and solubilised by weathering and biodegradative processes, the system approaches the status of an aqueous, single-phase flow. Leaching of hydrocarbons into surface and groundwater is primarily dependent upon the water-solubility of individual hydrocarbons, soil texture and the amount and intensity of rainfall. In good quality soils, leaching of undegraded hydrocarbons is minimal.

4.11 Oil Biodegradation Rates

Bearing in mind all the factors that could potentially influence oil biodegradation in soil, an attempt was made to correlate relevant field data:

Rates of Oil Mineralization in Soil

Type of Oil	Mineralization Rate [gHC(kg soil·day)]	Fertilizer	Reference
Crude oil	1.38	+	Schwendinger (1968)
Oily sludge	0.37	+	Kincannon (1972)
Oily sludge	0.18	-	Kincannon (1972)
Waste oil	0.60	+	Francke and Clark (1974)
Coolant	0.32	+	Francke and Clark (1974)
Gas oil	0.02	-	DeBorger et al. (1974)
Heavy fuel oil	0.11	-	Jensen (1975a)
Fuel oil	0.05	+	Lehtomäki and Niemelä (1975)
Waxy cake	0.004	+	Gudin and Syratt (1975)
Various oils	0.09 (max.)	+	Raymond et al. (1976)
Crude oil	0.08 (max.)	+	McGill and Rowell (1977)
Crude oil	0.02 (min.)	-	McGill and Rowell (1977)
Oily sludge	0.14	+	Dibble and Bartha (1979b)

Referring to the above table, assumptions and conversion factors made in the calculations were as follows:

1 Where sludges or emulsions were applied, numbers refer to net hydrocarbon concentration only.

2 When oil was applied per surface area, it is assumed to be evenly distributed in the upper 15cm (plough layer) of the soil; this was assured by repeated rototilling.

3 Specific weight of oils, when applied on per volume rather than weight basis, was assumed to be 1.0 (actually between 0.9 to 1.0).

4 Specific weight of all soils was taken as 1.5 (= average value for reasonably porous mineral soils). Therefore, the weight of 1ft^2 (900cm^2) soil to 15cm depth is 40kg (1m^2 = 225kg, 1 hectare = 2,250,000kg).

5 When oil biodegradation was calculated from carbon dioxide evolution, a 50% conversion efficiency was assumed (for every oil carbon conversion to biomass, another was incorporated into bacterial biomass) and oil was assumed to contain 85% carbon.

6 For year-round experiments in cool, temperate climates like Scandinavia, an actual growing season of 200 days was assumed.

All biodegradation rates are expressed as gram of hydrocarbon degraded per kg of soil per day. Application rates are given as a %w/w of hydrocarbon in soil. Rates listed in the table may be easily recalculated per surface units, and the number of kgs of hydrocarbon degraded per hectare per day may be obtained by multiplying the listed numbers by 2250.

Biodegradation rates in the table represent essentially ultimate biodegradation of hydrocarbons to carbon dioxide, water, microbial biomass and humus. They are based on the decrease of solvent-extractable material or on the evolution of carbon dioxide. One of the earlier studies (1968), based on the measurement of carbon dioxide evolved, showed a high, but unrealistic biodegradation rate, probably because the study did not include carbon dioxide evolution controls for uncontaminated soils.

4.12 Effects on Plants

As well as affecting the quality of the soil, indirect effects of petroleum pollution in soil include oxygen deprivation of plant roots, because of exhaustion of soil oxygen by hydrocarbon-degrading microorganisms. Such anaerobic conditions may bring about the microbial generation of phytotoxic compounds, such as hydrogen sulphide. Oil-degrading microorganisms compete with plants for mineral nutrients. Oil also affects the physical nature of the soil, decreasing its capacity to store moisture and air.

All these negative effects manifest themselves either immediately or during the biodegradation of the polluting oil. Once the biodegradation process of a moderate-size spill is complete, negative effects tend to disappear and soil may actually show an improvement in its ability to support plant growth compared with its pre-spill status. Such improvement is due to the increasing amount of organic matter and combined nitrogen in the soil after biodegradation of the spill. Severity and duration of the effects of a petroleum spill on a plant community are highly dependent upon the quality and quantity of spilled petroleum, the postspill treatment and soil type.

Measurement of biodegradation

Lubrizol Ecologically Responsive Technology

5.1 Introduction

There are several phenomena associated with biodegradation which can be measured:

Substrate loss

Formation of water or carbon dioxide as end products

Oxygen consumption

Release of energy , i.e. heat, or increasing number of bacteria.

The most logical means of measuring biodegradability is via substrate loss (i.e. via gravimetric analysis, total organic carbon, TOC, dissolved organic carbon, DOC, and quantitative IR.) Chemical Oxygen Demand, COD, forms part of the German water discharge law, but does not apply to water-insoluble substances, such as lubricants.

There is no test method available which takes all the important environmental criteria into account, i.e. water, soil, air and light.

A large number of tests are available for assessing "ready" and "inherent" biodegradability. To be considered readily biodegradable, a material must pass one of the more stringent OECD screening tests, indicating that it is likely to degrade rapidly and completely under aerobic conditions. A material which "fails" one of these tests may still be inherently biodegradable, and could degrade under more favourable conditions.

(i) Tests for "Ready Biodegradability"

Test conditions for these tests are deliberately severe. In general, ready biodegradation tests utilise the test material as virtually the sole nutrient in the test system, with low bacterial density and small substrate volume.

Many of the OECD screening tests require the material to be water soluble which restricts the tests available for lubricants. In a number of tests,

biodegradation is measured by comparing the amount of oxygen used to degrade the material (BOD) with either the amount needed to oxidise the material chemically (COD) or the theoretical oxygen demand (calculated from the molecular formula). The apparent resistance of many hydrocarbon-based lubricants to complete chemical oxidation, and the difficulties in defining their formulae, means that BOD/COD ratios are unlikely to provide meaningful results.

(ii) Tests for "Inherent Biodegradability"

Inherent biodegradation tests have quite high bacterial densities (inoculum concentrations), long residence time (time of direct contact), relatively high substrate concentrations and optimum adaptation conditions.

If no decomposition occurs in such a test, it can be taken that the substance is difficult to degrade biologically. If biological degradation does occur, it cannot be assumed that degradation occurs under the prevailing conditions of particular environments, since the test conditions are optimised to encourage the breakdown of the material under aerobic conditions.

Of the approved OECD tests for assessing ready biodegradability of lubricants, the MITI and modified Sturm tests are most useful, but the Closed Bottle test may be used in some instances. The CEC L-33-T-82 test is useful for assessing inherent biodegradation. Soil and anaerobic biodegradability tests may become more important in the future, and these are discussed later in this section.

5.2 Closed Bottle test

This is designed mostly for water-soluble compounds, and is in principle applicable to volatile and insoluble compounds. It measures the actual oxygen utilisation compared with theoretical expectations.

5.3 Modified MITI test

This is applicable for volatile compounds and for every kind of chemical in which $C_{water}/C_{air} > 1$. It measures the total oxygen consumed during all oxidation activities. Test material is transferred to a vessel containing a mineral substrate and bacterial inoculum. After ultrasonic vibration, the test vessel is closed and connected to an oxygen source. A control without the test material is run in parallel.

Oxygen consumption is measured continously by an automated closed system apparatus for measuring oxygen. Biodegradation is expressed as a percentage of the actual oxygen consumed by the test material during the test, (corrected for the control), against the theoretical oxygen demand required for complete oxidation.

The test is carried out at 25C and aniline is used as the reference fluid. For a valid test, aniline has to be degraded by at least 40% after 7 days, or 65% after 14 days. Test materials giving a result of more than 60% should be regarded as readily biodegradable. The test lasts 28 days and this level must be reached within 20 days of biodegradation exceeding 10%.

5.3 Modified Sturm test

The modified Sturm test is adequate for soluble and insoluble organic, non-volatile materials. This test measures carbon dioxide evolved and therefore measures only "complete" oxidation; organic impurities will complicate the interpretation of carbon dioxide production data.

Test material is introduced into a flask containing mineral substrate and a bacterial inoculum. After ultrasonic vibration, the flask contents are aerated with carbon dioxide-free air. A control without the test material is run in parallel.

Any carbon dioxide released is absorbed in flasks containing barium hydroxide solution. Periodically, the amount of barium hydroxide solution used is determined by titration with hydrochloric acid. Biodegradation is expressed as a percentage of the total amount of carbon dioxide evolved during the test, (corrected for the control), against the theoretical carbon dioxide that the test material could have produced.

The test is run at room temperature. Aniline is applied as a reference fluid to check the activity of the bacterial inoculum. A readily biodegradable fluid should have at least a 60% yield of carbon dioxide within 28 days. The test lasts 28 days and this level must be reached within 10 days of biodegradability exceeding 10%.

5.4 CEC L-33-T-82 test

The CEC test applies to most organic compounds, whether soluble or insoluble in water. It determines the overall biodegradability of hydrocarbons, or similar compounds containing (CH_2) methylene groups, measuring all transformations that the starting material undergoes, including oxidation and hydrolysis.

Test flasks containing mineral medium, test oil and inoculum are continually agitated at room temperature in the dark for 21 days.Samples are analysed at 0, 7 and 21 days. Flasks containing reference oil, together with poisoned flasks (containing mercury), are run in parallel. The reference controls used are:

White oil Enerpar M2632 ,	RL 130,	= 20-30% biodegradable
Di-*iso*tridecyladipate, DITA,	RL110,	= 100% biodegradable

At the end of incubation, contents of the flasks are subjected to sonic vibration, acidified and extracted using Freon (1,1,2-trichlorotrifluoroethane) Extracts are analysed by IR, measuring the 2930cm^{-1} (CH_2-CH_3) stretch. Absorption values are used to calculate residual oil contents of the poisoned and test flasks. Biodegradation is expressed as the % difference between residual oil contents of poisoned flasks and test flasks. Test repeatability is 10% absolute, reproducibility is 20% absolute, and the "pass" level ranges from 70 to 80%.

(i) CEC Test Acceptance

This test is most commonly used by the oil industry and is widely accepted.

It was developed to characterise the biodegradability of outboard engine oils on the Bodensee, due to the accumulation of mineral oils which tainted fish.

The CEC test is accepted in a number of Blue Angel Environmental Labels,

i.e. Readily biodegradable:

RAL UZ48	chainbar lube
RAL UZ64	lubes and mould oils
RAL UZXX	hydraulic
RAL UZYY	outboard engine oils

and requires 80% biodegradabilty. The German Blue Angel scheme does not intend to produce guidelines for "enclosed" systems. Categories for which this test is accepted by other bodies/countries are:

(i) Readily biodegradable outboard engine oils

ICOMIA 27-92 (Lube oil for 2-stroke cycle outboard engines-ecologically friendly)

Portugese Regulatory Decree nr. 37/91 (75% required)

(ii) Readily biodegradable grease:

DIN method, in preparation.

(iii) Norwegian environmental labelling scheme

(ii) Field Tests

The CEC L-33-T-82 test is the only biodegradability test to date which has shown field correlation.

ICOMIA (Motor Industry Environmental Protection Agency) looked into the practical relevance of the test. A motorboat travelled back and forth 600 times within 8 hours in a test tank filled with pure mountain stream water.

Morning: boat used synthetic oil, 1:100

Afternoon: boat used mineral oil , 1:50

Oil content in the water showed that the synthetic oil degraded immediately and was 95% eliminated at the end of test.; the mineral oil was only 50% biodegraded.

(iii) Limitations/ modifications to the CEC test.

Despite being convenient and easy, the CEC test only measures the IR absorbance of lipophilic molecules extractable into chloroalkane solvent. It does not measure the water-soluble metabolites which are poorly extractable and therefore, cannot measure extensive degradation or mineralisation. This would require a parallel test measuring oxygen consumption or carbon dioxide evolution. There is also no clear structural criterion which can be adopted to compare biodegradabilities of various structure types.

The CEC IL-24 Working Committee and PL-14 Working Group recently proposed amendments to the test at a joint meeting in Hamburg in September 1992. Further amendments are still necessary, but the immediate intentions are to:

1 Extend applicabililty of the test method to include transmission and hydraulic fluids

2 Investigate the use of alternative dip slides to identify fungi and mixed microbial cultures in addition to colony count

3 Include a terminology section defining relevant terms used throughout the method

4 Provide new names for reference samples, as well as addresses where they can be obtained readily. This follows a reported batch variation of RL 110 (white oil), which affected biodegradability by about 10%.

At the last CEC IL-24/PL-14 combined meeting (19th November 1992), it was stated that carbon tetrachloride would no longer be acceptable, and that CEC L-33-T-82 should be viewed as a screening method only,since it measures

potential, not absolute biodegradability, and gives no rate of biodegradation information.

5.6 Test method correlation

Recently, good correlation was shown between biodegradation in the CEC test and biodegradation in a modified Sturm test which measures ultimate biodegradation; the study used 39 base oils, formulations and pure compounds.

One of the samples considered was DITA, (the ester of adipic acid and *iso*tridecanol, a highly branched alcohol). DITA mineralisation was much lower than that predicted by the model based upon DITA's high biodegradability in the CEC test. In general, the extent of biodegradation in the modified Sturm test was lower than in the CEC, since the Sturm test measures the mineralisation of the product through to carbon dioxide. The CEC test measures the loss of material that can be extracted from the aqueous phase with either chloroform or Freon. Metabolites may be resistant to further degradation.

BP have ranked the reliability of biodegradation tests in descending order as follows:

1 Biodegradation tests of > 28 days using radiolabelled test chemicals

2 Tests using highly specific analytical techniques for parent compounds

3 Tests using non-specific analytical techniques:

- (i) CO_2 evolution
- (ii) Loss of DOC
- (iii) BOD (O_2 uptake)

The ranking is relative; 5-Day BOD values may be highly reliable if they show high biodegradability, and tests results from intact original samples are more reliable than those from composite samples.

5.7 Soil Biodegradability

The CEC intends to develop a suitable test method for inherent soil biodegradation, and it was recently proposed that a single soil type of pH4 and a temperature of 20C be used, measuring the oxygen uptake or carbon dioxide evolution.

Various soil types can be used to determine the actual theoretical carbon dioxide yields from known loadings of test materials. Although radioactive tracing is utilised, it is not essential. Oil biodegradation has been observed by indirect methods, e.g. by an increasing number of oil-degrading microorganisms after pollution, and/or characteristic changes in oil composition, e.g. a decrease of n-alkane ratio as compared to branched pristane or phytane. Direct measurement is preferable however.

Biodegradation of individual hydrocarbons or of petroleum in soil is commonly measured by periodic extraction of incubated replicate soil samples with an organic solvent, e.g. diethyl ether or methylenechloride. Exhaustive solvent extraction is typically performed in a Soxhlet apparatus or similar continuous extraction device. Solvent extract is evaporated in a tared dish and the residual weight of hydrocarbon is determined gravimetrically. Solvent extract contains not only polluting fossil hydrocarbons, but also lipids, waxes, and hydrocarbons of nonfossil origin. In mineral soils, 1 to 5%, and in peat soils, up to 20% of organic matter may be extracted by organic solvents. Thus, uncontaminated soil controls need to be extracted and used for correction whenever residual weight is used as a measure of fossil hydrocarbon

biodegradation. Extracted biodegradation intermediates contain oxygen. The added weight of oxygen causes some underestimation of the actual hydrocarbon biodegradation. Hydrocarbon loss may occur by abiotic mechanisms, primarily by evaporation. Sterile or poisoned controls, e.g. with 1% $HgCl_2$, need to be included if the net biodegradation losses are to be determined.

5.8 Anaerobic Biodegradability

This is important for compounds of low solubility and high absorbancy. Biodegradation under anaerobic conditions takes place through stages in which several different groups of bacteria participate in the ultimate production of carbon dioxide and methane. Anaerobic ultimate degradation can therefore be determined by measuring this gaseous end product.
An example of this test procedure is the simulation test of a sewage plant digestion sludge requiring marked radioactive test material. There is also a recently developed anaerobic screening test for routine research (ECETOC test), in which a range of natural oil-based products are also tested.
The results obtained with some ester oils show that such compounds are anaerobically readily degradable. This is connected to the fact that ester compounds have a "predetermined breaking point" for bacterial attack which does not require molecular oxygen during the initial stage of degradation.

COMPARISON OF BIODEGRADABILITY TESTS FOR OIL-SOLUBLE LUBRICANTS

Test	Aeration Method	Test duration, days	Temp, C	Sample concentration, mg/l	Inoculum, CFU	Inoculum source	Medium	Biodegradation parameter	Pass criteria
CEC L-33-T-82	Shaken	21	25	50	10^6	Sewage effluent	Nutrient solution	IR absorption CH_2-CH_3 loss	70- 80% loss
Mod. Sturm OECD 301B	Blowing air	28	20- 25	10 -20	10^6 to 20 x 10^6	Sewage effluent	Nutrient solution	CO_2 released/ DOC	60% CO_2 within 28 days
Mod. MITI OECD 301C	Stirring	28	20- 25	100	10^7- 10^8	Mixed sewage from 10 different plants	Nutrient solution	O_2 depletion/ DOC	Degradation to 60% of BOD in 28 days (70% loss of parent compound)
Closed Bottle OECD 301D	Saturate with air	28	20	2 to 10	10^4- 10^6	Mixed inoculum from specified sources	Nutrient solution	O_2 depletion	60% of theoretical O_2 demand in 28 days

APPENDIX I:

Structure Activity Relationships for the Prediction of Biodegradability of Environmental Pollutants

Structure Activity Relationships (SARs) are emerging as a valuable tool in predicting the toxicity and environmental fate of pollutants. Due to the costly and time-consuming nature of the testing methods, SARs are being used effectively in setting standards for existing pollutants in the environment. SARs can provide qualitative information as to how modification of chemical structures results in changes in chemical or biological activity.

However, the application of SARs in the prediction of biodegradability of environmental chemicals has only been evaluated in recent times. Information on the environmental pathways and distribution often requires the development of Quantitative Structure Activity Relationships (QSARs) between the fundamental quantitative characteristics of chemicals and their activity. These mathematical relationships may be derived either experimentally or theoretically, based on the structure of the chemical. QSARs supplement and extend, rather than replace, the experimental investigation of the environmental fate of a chemical.

There are a range of processes in the environment involved with overall biodegradation of a chemical, any one of which may be rate determining. The development of QSARs for biodegradation will be facilitated if one of the processes is rate determining or dominant. Development of QSARs for biodegradation often utilises the first or second order rate constants as biodegradation characteristics.

The kinetics of biodegradation generally are represented by Monod's equation for microbial growth:

$$V = V^*[S] / (K^* + [S])$$

where:

V and V*	=	actual and maximum growth rates
K*	=	substrate concentration required to reach half the maximum rate
[S]	=	substrate concentration

Due to the complexities involved, most of the relationships which have been developed for biodegradation are qualitative or semi-quantitative in nature. Development of quantitative relationships between molecular characteristics and biological activity requires a large and self-consistent data base. Most of the studies on SARs have expressed the biodegradation in terms of BOD, chemical oxygen demand (COD), and the first and second order rate constants. A major problem in the development of a large biodegradation data base is that different sets of data have been obtained using different experimental procedures under a wide range of conditions. Often different experimental methods result in widely varying results for the same compound. Hence, it is often difficult to collate the data into a consistent data base.

APPENDIX II:

Bioremediation

Bioremediation is the controlled use of biodegradation to remove toxic chemicals from the soil and groundwater. All bioremediation techniques involve using microorganisms to degrade the pollutants, and the use of microorganisms has emerged as one of the most promising technologies for treating contaminated groundwater. Blends of microorganisms are used to degrade petroleum hydrocarbons either aerobically or anaerobically.

Microorganisms are very versatile, and can be quite efficient at degrading toxic compounds. Despite its cost-effectiveness, bioremediation is the least developed treatment technology, although a number of promising site studies and other research activities have been done. The microorganism is selected to metabolise (or at least oxidise) the target contaminant under the conditions in the contaminated site, or in an above-ground reactor. Sometimes, enzymes used for degradation of the target contaminant are not induced by the presence of the pollutant, either because the concentration is too low or because of the xenobiotic nature of the compound. In such cases, cometabolism may be helpful.

Success of bioremediation depends upon the same factors that affect biodegradability, i.e. soil permeability, oxygen supply, toxicity and concentration of contaminants, concentration and types of nutrients, pH (optimum at 6.5 to 7.5), other organics, microorganisms, temperature (optimum at 10 to 35C), and the presence of bulking agent (when using above-ground reactors). Chlorinated hydrocarbons may be degraded, the ease of biodegradation decreasing as the number of chlorine atoms per molecule increases. Highly concentrated organics, e.g. PCB's, chloroform,

carbon tetrachloride, tetrachloroethylene, trichloroethylene and dichloroethylene are not readily biodegradable aerobically and are toxic in concentrations of mg/litre. In general, relatively simple compounds , e.g short chain hydrocarbons, alcohols, phenols and other small molecules are relatively easy to degrade, while larger and more highly substituted compounds are more difficult.

Chemical structure also influences the density of adsorption of the compound onto soil particles. Such adsorption may be a problem when using above-ground reactors. Typically, "stubborn" compounds are also quite hydrophobic and adsorb readily onto inert solids. Thus, they are difficult to flush out of the aquifier under standard conditions and *in situ* biodegradation may be the only technically and economically feasible way to achieve remediation.

APPENDIX III:

Lubricant Wastage Disposal/ Environmental Accumulation

In 1990, the total sales of lubricant within the EEC totalled 4.5 million tonnes. This was disposed of as follows:

2.45 million tonnes	fully consumed
700,000 tonnes	reprocessed
750,000 tonnes	fuel
600,000 tonnes	"disappear"

In Germany alone, 40,000 tonnes of loss lubricants were directly discharged into the environment, i.e. mould release agents, corrosion protection agents, chain saws, shunts/wheel flange lubes, 2-stroke engine oils, wire rope lube, open gear and compressed tool lubes. For example, 5,000 tonnes of chainsaw lube were lost into the German forests and 10-30% of hydraulic oils was lost through leakage and/or accident. In addition to this, about 2000 tonnes of lube oil remained in emptied casks and approximately 10,000 tonnes of used oil were removed haphazardly.

46,000 tonnes of gear oils were lost during use and 19,000 tonnes of metal-working fluid either adhered to work pieces or were produced as retention from emulsion in an ultra-filtration separator. 103,000 tonnes i.e. 90% of air filter oils, heat transmission fluid, print colour oils, oleo oils and scavenge oils were further lost into the environment.

REFERENCES

General

1 "Environmentally considerate lubricants for the automotive and engineering industries", S.J. Randles/ A.J. Robertson/ R.B. Cain, (Aug 1990)

2 "The quest for environmental products", Marsh Hardin, *INFORM*, **2(10)**, (Oct 1991)

3 "Designing biodegradable molecules for the oleochemical industries", R.B. Cain (1990).

4 "Biodegradability of engine oils", Owen W.M. Marsh (Esso Research Centre), *SIA 1992 Conference paper*, July 1992.

5 "Biodegradable lubricants that are environmentally safe for forests and water", *Tribologie and Schmierungstechnik*, **35(3)**, 118-24, (1988)

6 "Solution of ecological problems in development and application of motor oils", V.A. Zolotov/ V. L. Lashkhi, translated from *Khimiya Tekhnologiya Topliv i Masel*, **7**, 2-3, (July 1990)

7 "Biodegradation of oil and bioremediation of oil spills", Ronald M. Atlas/ Michael C. Atlas, *Current Opinions in Biotechnology*, **2(3)**, 440-3, (Jun 1991).

8 "Microbial degradation of hydrocarbons in the environment", Leahy, J.G./ Colwell, R. R., *Microbiological Reviews*, **54(3)**, 305-315, (1990)

9 "Reducing the stresses on the environment through biologically fast degradable lubricants", Workshop 7th June 1990, Bonn.

10 "Biodegradability: an issue for future petrochemicals", *Hydrocare Process*, **67(13)**, Oct 1988.

11 "Design guidelines for biodegradation of specific organic pollutants in petroleum refinery wastewaters", *ASME Industries Pollution Control Symposium*, Dallas, 69-76, (Feb 17-21, 1985)

12 "Means of disposal for biodegradable lubricants", U. J. Moller, Burmah Oil Deutschland

Microorganisms

13 "Biological damage to lubricants", E. Toropova et al., Lomonosov Moscow State University, Gubkin Moscow Institute of Oil and Gas (MING), translated from *Khimiya i Tekhnologiya Topliv i Masel*, **11**, 22-24, (Nov 1988)

14 "Microbial oxidations of fatty alcohols and fatty acids", Colin Ratledge, University of Hull, (1990)

15 "Distribution and biodegradation potential of oil-degrading bacteria in N. Eastern Japanese coastal waters", Venkateswaran, K. et al., FEMS (Federal European Microbiological Society), *Microbiol. Ecol.*, **86(2)**, 113-22, (Dec 1991)

16 "Oil pollution experiments in marine-enclosed experimental ecosystem, I. Ecological distribution of hydrocarbon-degradation bacteria", Zhou, Z./ Ni, C./ Cai, Z./ Zeng, H., *Acta. Oceanol. Sin.*, **10(2)**, 297-302, (1991)

17 "Biodegradation of crude oil hydrocarbons in water environment", Miklosovicova, L./ Trzilova, B., *Biologia (Brastisl)*, **46(3)**, 219-28, (1991)

18 "Biodegradation of phthalates and their esters by bacteria. Environmental health perspectives", Keyser, P./ Basayya, G., et al., ICI Automotive and Engineering Group, **18**, 159-166, (1976)

19 "Microbial degradation of hydrocarbons in the environment" Leahy, J. G./ Colwell, R. R., *Microbiol. Rev.*, **54(3)**, 305-15, (Sept, 1990)

20 "Microbial degradation of petroleum hydrocarbons: an environmental perspective", Ronald M. Atlas, *Microbiol. Rev.*, **45(1)**, 180-209, (1981)

Viscosity Effects

21 "Effect of viscosity on the biodegradation of automotive lubricating oils", O.O.Amund/ A.G. Adebiyi, *Tribology International*, **24(4)**, 235-237 (Aug 1991).

Biodegradation of Used Oil

22 "Influence of physico-chemical stress on biodegradability of car engine lubricating oil", G.C. Okpokwasili/ B.B. Okorie, *International Biodeterioration*, **27**, 255-264, (1990).

23 "Biodeterioration potentials of microorganisms isolated from car engine lubricating oil", G.C. Okpokwasili/ B.B. Okorie, *Tribology International*, **21(4)**, 215-220, (Aug 1988).

Additive Effect

24 "Effect of Emulsan on biodegradation of crude oil by pure and mixed bacterial cultures", Julia M. Foght/ David L. Gutnick/ Donald W. S. Westlake, *Applied and Environmental Microbiology*, **55(1)**, 36-42, (Jan 1989)

25 "The environmental fate of fatty acid α-sulphomethyl esters", Josef Steber/ Peter Wierich, abridged version of an article in "*Tenside Surfactant Detergents*", **26**, 406, (1989)

26 "Surfactants: focus on the environment", Andrew Wood, *Chemical Week*, **30**, (Jan 29, 1992)

27 "Biodegradation of halogenated organic compounds", G. Rasul Chaudhry/ S. Chapalamadugu, *Microbiological Reviews*, **55(1)**, 59-79, (March 1991)

28 "The biodegradation of halogenated organic compounds", A. H. Neilson, *J. Appl. Bacteriology*, **69**, 445-470, (1990)

29 "The environmental microbiology of chlorinated aromatic decomposition", Michael Boyle, *J. Environmental Quality*, **21(4)**, 395-402, (Oct/Dec 1989)

30 "Biodegradation of toxic and environmental pollutants", Lilly Y. Young/ Max M. Haggblom, *Current Opinion in Biotechnology*, **2(3)**, 429-435, (June 1991)

Toxicological Assessment

31 "Use of biodegradation data in chemical assessment", *Environmental Toxicology and Chemistry*, **9**, 1369-1377, (1990).

32 "Chemical fate of toxic substances: biodegradation of petroleum", J. D. Walker, bibl., (80-86), *Marine Technology Soc. Journal*, **18(3)**, 73-86, (1984)

33 "Evaluation of toxicity of substances to be assessed for biodegradability", *Technical Report No. 23*, ECETOC Secretariat, Bruxelles, 1-32, (Nov 1986)

Freshwater

34 "The fate of petroleum pollutants in freshwater ecosystems in petroleum microbiology", Cooney, J. J., edited by Atlas, R. M., 399-433, MacMillan Pub. Co., New York, (1984)

Sea

35 "Effect of salinity on biodegradation of oil spill dispersants", G. C. Okpokwasili/ L. O. Odokuma, *Waste Management*, **10**, 141-146, (1990)

36 "Biodegradation of petroleum hydrocarbons under tropical estuarine conditions", O. O. Amund/ C. O. Igiri, *World Journal of Microbiology and Biotechnology*, **6**, 255-262, (15 Nov 1990)

Soil

37 "Biodegradation of synthetic lubricants in soil", S.D. Haigh, abstract from PhD thesis, Dept. of Agricultural and Environmental Science, Univ. of Newcastle-upon-Tyne, (1989)

38 "Fate of petroleum in soil ecosystems", Bossert, I./ Bartha, R., in *Petroleum Microbiology*, edited by Atlas, R. M., 434-476, MacMillan Pub.Co., New York, (1984)

39 "Improving microbial degradation of oil in soil", Lehtomaki, M./ Niemela, S., *Ambio*, **4(3)**, 126-129, (1975)

40 "Fate of hydrocarbons during oily sludge disposal in soil", Bossert, Ingeborg/ Wayne, M. Kachel/ Richard Bartha, *Appl. and Env. Microbiol.*, **47(4)**, 763-767, (1984)

41 "Adsorption of polycyclic aromatic hydrocarbons (PAH's) by soil particles: influence on biodegradability and biotoxicity", Weissenfels, Walter, D./ Hans-Jurgen Klewer/ Joseph Langhoff, *Appl. Microbiol. Biotechnol.*, **36**, 689-696, (1992).

Biodegradability Testing

42 "Biodegradability of non-ionic surfactants: screening test for predicting the rate and ultimate biodegradation", R. N. Sturm, *J.Am. Oil Chem. Soc.*, **50**, 159-167, (1973).

43 "A correlation between the biodegradability of oil products in the CEC L-33-T-82 and modified Sturm tests", N. S. Battersby/ S. E. Pack/ R. J. Matkinson, *Chemosphere*, **24**(12), 1989-2000, (1992)

44 "The status of the CEC biodegradability test CEC L-33-T-82", T.F. Bunemann (Chairman CEC IL-24), International Congress Brussels, Sept 16-18, 1992 from "Lubricants of the future and environment"

45 "Report on the ecotoxicological effects of lubricants in soil", Wolfgang Ahlf/ Judith Gunkel, Technical University Hamburg, (April 1992)

46 "Biodegradability of 2-stroke cycle outboard engine oils in water", CEC L-33-T-82 test method

47 "Biodegradability of vegetable oils and raw materials", J. Steber, Henkel report

48 "The use of laboratory techniques to simulate biodegradation of lubricants in the environment", A.J. Robertson/ S.J. Randles, Automotive and Engineering Industry Group, ICI Chemicals and Polymers, Wilton, (1990)

49 "Biodegradable lubricants: test materials and applications", D. Kenbeek/ G. van der Waal, *Unichema International*, (June 1992)

50 CEC L-33-T-82 amended method (proposed amendments to method made by CEC IL-24 sub-committee; meeting held at BP Hamburg, 28/9/92), Esso Petroleum Group, Abbingdon, UK.

51 "A comparitive study of test methods for assessment of the biodegradability of chemicals in seawater - screening tests and simulation tests", *Ecotoxicology and Environmental Safety*, **23**, 173-190, (1992).

52 "Biodegradability testing for synthetic esters", Versino, C./ Novario, M., *Journal of Synthetic Esters*, **4(1)**, 3-23, (1987).

53 "Solid-phase extraction for toxicity reduction evaluations of industrial wasterwater effluents", Martha, J.M. Wells/ Anthony J. Rossano, Jr./ Eugene c. Roberts, *Analytica Chimica Acta*, **236**, 131-139, (1990).

54 "On the biodegradability in waste water management. Is the Zahn-Wellens test the suitable test?", Schonberger, H., Z. *Wasser Abwasser Forsch*, **24(3)**, 118-28, (1991)

55 "Biodegradation testing: an assessment of the present status", *Technical Report No. 8*, ECETOC Secretariat, 1-19, (Nov 1983)

56 "Biodegradation tests for poorly-soluble compounds", *Technical Report No. 20*, ECETOC Secretariat, 2-21, (Feb 1986)

CEC Test Acceptance

57 "Draft of the basis for according the environmental mark to biologically quickly degradable lubricants and forming oils", Federal Department of the Environment, I 1.1-90081-1/122, Berlin, (July 1990)

58 "Screening methods for assessment of biodegradability of chemicals in seawater - results from a ring test", *Ecotoxicology and Environmental Safety*, **23**, 161-172, (1992).

59 Various minutes from the CEC IL-24 and PL-14 group meetings.

60 "Analysis of the results of the CEC Biodegradability Round Robin Test", Green Tech Research SPRL, Nov 1991 (correspondence from P. van Donkelaar to BDL)

61 "Field tests on the fate of 2-stroke lubricants in water resulting from intensive outboard motor operation", Wachs, B/ Wagner, H., ICI Automotive and Engineering Industrial Group, **23(11)**, (1990).

62 "Two-stroke engine lubricant emissions in a body of water subjected to intensive outboard motor operation", Bodo Wachs/ Helmut Wagner/ Pieter van Donkelaar, Report by Greentech Research Sprl., (30th April 1991)

63 "Preliminary draft of the conditions for awarding the environmental badge for biologically fast degradable hydraulic fluids", Federal Environmental Office, Berlin, I.1.1-9081-1/148, (Sept 1990)

Bioremediation

64 "Biological remediation of shoreline oily waste from marine spills", *Env. Canada Arctic and Marine Oil Spill Program, 13th Technical Seminar*, Edmonton, AB, 387-399, (June 6-8, 1990).

65 "Biological treatment of soils contaminated by petroleum products", Univ of Massachusetts, *Petroleum Contaminated Soils, 4th National Conf.*, Amherst, **3**, 167-175, (Sept, 1989)

66 "Bioremediation of oil-contaminated land", Ellis, B./ Balba, M. T./ Theile, P., *Environ. Technol.*, **11(5)**, 443-55, (May 1990)

67 "Bacteria used to clear up oil field sumps", *Manage. World Wastes*, **27(6)**, 6, (Dec 15, 1984)

68 "Pilot remediation tells all about petroleum contaminated soil", Michael J. Barnhart/ Julian M. Myers, *Pollution Engineering*, 110-112

69 "Microorganisms get to work", Gary F. Bennett/ Kevin P. Olmstead, *Chemistry in Britain*, 133-137, (Feb 1992)

70 "Rapid biological clean-up of soils contaminated with lubricating oil", B. E. Rittmann/ N. M. Johnson, *Water Science and Technology*, **21**, 209-219, (1989)

LUBRIZOL INTERNATIONAL LABORATORIES
THE KNOWLE, NETHER/ LANE/HOB HILL, HAZELWOOD,
DUFFIELD, BELPER, DERBYSHIRE DE56 4AN, UK
TELEPHONE 0332-842211
TELEX 37445
FAX 0332-842303

MAILING ADDRESS:
LUBRIZOL INTERNATIONAL LABORATORIES
PO BOX 88, BELPER, DERBY DE56 1QN, UK

Lubrizol Hazelwood job number 1704
Printed in England

LUBRIZOL